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NRC. DIVISION OF CHEMISTRY AND  
CHEMICAL TECHNOLOGY.  
**ANNUAL SURVEY OF  
AMERICAN CHEMISTRY**

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**VOLUME X  
1935**

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Published for  
**THE NATIONAL RESEARCH COUNCIL**  
BY  
**REINHOLD PUBLISHING CORPORATION**  
330 WEST 42ND STREET, NEW YORK, N. Y.  
1936

QD1  
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INTERNATIONAL TEXTBOOK PRESS  
SCRANTON, PA.

## FOREWORD

With this volume, the Annual Survey completes the first decade of its existence, the ten volumes covering the period 1925 to 1935, inclusive. During this time an endeavor has been made to cover, as completely as possible, the progress made in American Chemistry, and to indicate, by implication if not by actual statements, the trends in the various fields of pure and applied chemistry in the United States. The favorable reception of the Survey leads us to believe that we have accomplished these objectives as well as may be expected in a volume of this size.

Any measure of success, however, is due entirely to the cordial and unselfish cooperation of the many authors who have, in the various volumes, given of their time, knowledge and experience in the preparation of their respective Chapters and it is a pleasure to acknowledge this cooperation and to thank them for their contributions. Each chapter represents many hours of thoughtful reading before a word can be written, to say nothing of the time required to coordinate the hundreds of papers into a unified whole.

Of the twenty-five chapters this year, twelve may be considered to be devoted to industrial topics. This number is the same as last year, although the subjects covered are quite different.

The Editor wishes to express his thanks to the Editorial Board (F. W. Willard, P. H. Emmett and R. S. McBride) for the thought given to the preparation of the Table of Contents and the selection of authors; also, to Miss Callie Hull, for her assistance in checking the thousands of references found in the present volume and in the reading of the proof, and to Miss Marion E. Jackson, for the preparation of the Author Index.

CLARENCE J. WEST

Washington, D. C.,  
May 18, 1936.



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# Chapter I.

## Theories of Solution.

HERBERT S. HARNED AND BENTON B. OWEN,  
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**General.** Two contributions to the general theory of chemical statics and dynamics published during the year 1935 should receive the closest attention of those interested in the interpretation of the properties of condensed phases. The first is a general development of the statistical mechanics of fluid mixtures by Kirkwood<sup>69</sup> by a method which possesses both power and simplicity. The second is a general theory of reaction velocity by Eyring,<sup>23</sup> in which the nature of the intermediate activation complex in chemical reaction is interpreted.

Kirkwood's treatment of the statistical mechanics of gas mixtures and solutions is based upon a principle clearly stated by Onsager that the parameters necessary to express the potential of intermolecular forces have the same status as the parameters of external force, and may be manipulated in the same manner. This principle is not restricted to any kind of intermolecular force. Indeed, it is possible to introduce arbitrary parameters for the potential of intermolecular force by means of which the coupling between molecules may be varied in any convenient manner.

Upon this very general basis Kirkwood has obtained expressions for the chemical potentials of the components of fluid mixtures in terms of comparatively simple integrals of the configuration spaces of molecular pairs. These integrals have been studied comprehensively, the equation of state of a real gas mixture discussed, and a molecular pair distribution function for dense fluids computed. The value of obtaining a powerful theoretical approach to the statistics of condensed systems cannot be overestimated, and this is probably the best method of treatment yet suggested.

Eyring's theory of reaction velocity is based upon the consideration that the forces between atoms are due to the motion and distribution of electrons and therefore must be computed by quantum mechanics. If these forces have been computed, it can be assumed that the nuclei of the atoms in this force field move according to classical mechanics. Thus, if the forces are known,

it becomes possible to compute reaction velocities according to the classical methods of statistical mechanics, such as those developed by Herzfeld, Tolman, Fowler, and Pelzer and Wigner.

A group of atoms may arrange themselves in an infinite number of ways. If the energy of such a system for the lowest quantum state of electrons be plotted against the distance between nuclei, a potential surface is obtained which determines the motion of the nuclei. Low places on such surfaces correspond to compounds, and these are the more stable, the higher the pass over which the atoms must move in order to get to another stable state. A reaction corresponds to the passage of the system from one to another of these low regions of potential, and it is certain that this process shall take place by way of the lowest pass. The "activated state" is the highest point along this lowest pass.

According to this definition, the activated complex is described by a saddle point with positive curvature in all degrees of freedom except the one which corresponds to crossing the barrier. These barriers are flat near the top. According to this picture of the activated state, it appears that the activated complex is represented by a configuration of atoms corresponding to a stable compound, except in the mode which corresponds to decomposition, and this mode, because of the small curvature of the barrier, may be treated as a single translational degree of freedom by the classical mechanics. This idea is the most important innovation of Eyring's theory. Upon this basis, the calculation of the concentration of the "activated complex," and subsequently the reaction velocity constants for reactions of different types, can be achieved by straightforward statistics and will not be described here.

**Reaction Velocities in Liquid Systems.** The theory of reaction rates developed by Eyring leads to the following equation for the velocity constant,  $k'$ ,

$$k' = \kappa K^{\ddagger} \frac{kT}{h} \quad (1)$$

where  $\kappa$  is a transmission coefficient,  $K^{\ddagger}$  a dissociation constant between the activated complex and the reactants, and  $\frac{kT}{h}$  a universal frequency,

since  $k$  is Boltzmann's constant and  $h$  is Planck's constant.  $\kappa$  is of the order of unity, except in cases where the reaction is one of adsorption on a solid surface, in which  $\kappa$  can be identified with the accommodation coefficient. Wynne-Jones and Eyring<sup>156</sup> have applied this theory to reaction velocities in condensed phases. They have shown that Brönsted's equation is a special case of the theory. Their views of the critical complex agree closely with the original interpretation of Brönsted, since they come to the conclusions that the intermediate complex is of extremely short life ( $\sim 10^{-13}$  secs.), and that the activity coeffi-

cient factor is essentially thermodynamic in character, or that the activity coefficient of the activated complex is a thermodynamic quantity. This differs from the conclusion of La Mer who regarded this quantity as possessing kinetic and not thermodynamic significance.

It is important to note that equation (1) possesses characteristics similar to those derived by different methods by other investigators.<sup>78, 113, 114</sup> Since  $K^\ddagger$  is an equilibrium constant, equation (1) may be written

$$k' = \kappa e^{-\frac{\Delta F^\ddagger}{RT}} \frac{kT}{h} = \kappa e^{-\frac{\Delta H^\ddagger}{RT}} e^{-\frac{\Delta S^\ddagger}{R}} \frac{kT}{h} \quad (2)$$

where  $\Delta F^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  are free energies, energies, and entropies of activation. We note in particular that the appearance of an equilibrium constant in equation (1) brings out the importance of a free energy of activation in the expression for the reaction rate, a conclusion previously reached by an entirely different procedure by La Mer.<sup>78</sup>

Eyring's theory of absolute rates has been discussed by Rodebush,<sup>110</sup> and by Kassel,<sup>66</sup> and contrasted with the theory of Rice and Gershinowitz by these authors.<sup>113, 114</sup> A similar theory has also been developed by Evans and Polanyi.\* Wynne-Jones and Eyring have applied the theory to some cases of monomolecular and bimolecular reactions, and to acid and base catalysis in solution.

La Mer and Kamner<sup>80, 81</sup> and La Mer and Miller<sup>83</sup> have studied the temperature dependence of the entropy and energy of activation. They employed the equation

$$\log k = B - \frac{E_{act}}{2.3 RT}, \quad (3)$$

where  $k$  is the velocity constant,  $E_{act}$  is the energy of activation, and  $B$  is associated with the entropy of activation. La Mer and Kamner<sup>80</sup> studied the effect of electrolytes on  $E_{act}$  and  $B$ . By combining Brönsted's reaction velocity equation and Debye's limiting law for activity coefficients, they obtained the limiting laws for the variation of  $B$  and  $E_{act}$  with ion concentration in the forms,

$$E_{act}/2.3 RT = E_{act}^0/2.3 RT + 0.51 z_A z_B \sqrt{\mu} \quad (4)$$

$$B = B^0 + 1.52 z_A z_B \sqrt{\mu} \quad (5)$$

Thus, the square root of the  $B$  varies three times as rapidly as  $E_{act}$  with ionic strength of the solution. La Mer and Kamner<sup>80</sup> computed  $B$  and  $E_{act}$  for the reaction between bromoacetate and thiosulfate ions, and found that these quantities vary with temperature. They<sup>81</sup> also studied the influence of non-electrolytes upon the velocity constant of this reaction. They found that the constant  $B$  varies almost linearly

\*Evans, M. G., and Polanyi, M., *Trans. Faraday Soc.*, **35**: 875 (1935).

with the reciprocal of the dielectric constant. La Mer and Miller<sup>83</sup> have made an extended study of the effect of temperature upon the velocity of dealdolization of diacetone alcohol catalysed by hydroxyl ion. They found that the energy of activation is a function of the temperature. All these results bear out the contention that both the energy and entropy of activation are important in interpreting the kinetics of chemical reactions in solution.

If at constant composition, the velocity constant is taken to be a function of the dielectric constant and the temperature, Svirbely and Warner<sup>132</sup> have shown that

$$(E)_N = (E^*)_D + 2.3 RT^2 \frac{\partial \log k}{\partial D} \frac{dD}{dT}, \quad (6)$$

where  $(E)_N$  and  $(E^*)_D$  are critical increments (free energies of activation) in a solvent of fixed composition, and in a medium of fixed dielectric constant,  $D$ , respectively.  $E$ , not  $E^*$ , should be considered true critical increments. Svirbely and Warner used this idea, combined with the Brönsted equation, and Scatchard's equation for medium effects on reaction velocities, to derive equations for the influence of dielectric constant and ionic strength on critical increments. The predictions are in good agreement with observed results of the reaction between ammonium and cyanate ions over a considerable temperature range, and in water-methyl alcohol mixtures at dielectric constants of 63.5 and 55.0. Part of the experimental results used in this computation were obtained by Warner and Warrick.<sup>145</sup>

Sturtevant<sup>130</sup> has extended Christiansen's treatment of the theory of bimolecular ionic reactions by taking into account the possibility of orientation effects. He obtains a solution for the case in which one of the ions is assumed to be a prolate spheroid. The result shows that electrostatic orientation effects in reactions between the ions are negligible in dilute solution, and that deviations from Brönsted's equation must be attributed to other causes.

The velocities of the reactions of sodium bromomalonate and bromosuccinate and the thiosulfate ion have been determined by Bedford, Austin and Webb<sup>6</sup> at different temperatures. The results are not in accord with Brönsted's theory. The discrepancy was attributed to orientation effects.

Straup and Cohn<sup>129</sup> have measured the rates of reaction of the thiosulfate ion with the uncharged molecule of ethyl iodide and bromoacetate ions in aqueous solutions containing urea, ethyl iodide, and amino acids. The rates of reaction with the uncharged molecule are increased by alcohol, and to a small extent by urea, and decreased by ions and amino acids. The rate of reaction with ions is increased by the presence of ions and urea, but decreased slightly by alcohol. The effect of change of media upon these reaction velocities is not due entirely to the change in dielectric constant. In the presence of

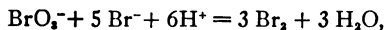
the amino acids the results may be accurately computed by the velocity equations of Kirkwood, which the latter developed by the Brönsted-Christiansen method from his theoretical treatment of activity coefficients of amino acids.

Further study of the decomposition of nitramide in acid and acid-salt mixtures has been carried out by Marlies and La Mer.<sup>98</sup> The technique, both of preparation of the nitramide and measurement of its decomposition, has been improved to the extent that the accuracy is about 1 percent. A negative primary salt effect was found and was attributed to the influence of the salts on the catalytic activity of the base, water. The evidence indicates a small acid catalysis which had not been observed by earlier investigators of this reaction. The mechanism of the reaction has been discussed, and a mechanism for the acid catalysis proposed. If a catalysis by the hydroxide ion be assumed, then the catalytic constant for this ion is about 2,000 times that of any other ion yet studied. A lower velocity is obtained in heavy water than in ordinary water.

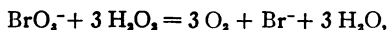
The velocity of inversion of sucrose catalyzed by strong acid solutions has been investigated by Krieble.<sup>74</sup> The velocity constants are not functions of either the activity or concentration of the hydrogen ion. The suggestion was made that both the hydrogen ion and hydrochloric acid molecule, or both ions, act as catalysts. On this basis, the velocity constants for hydrochloric and hydrobromic acid as catalysts may be expressed as a function of the activities. Krieble and Reinhart<sup>75</sup> have determined the activity coefficient of hydrochloric acid at high concentrations in water and sucrose solutions. A definite relationship between the velocity constant of inversion of cane sugar and these activities was noted. The velocity constant of cane sugar hydrolysis, catalyzed by acids and by invertase, has been investigated by the dilatometric method by Hitchcock and Dougan.<sup>55</sup> The values obtained for the acid hydrolysis agreed closely with those determined polarimetrically. The effects of sucrose concentration and  $pH$  upon the velocity of the invertase reaction, determined dilatometrically, were in agreement with those evaluated polarimetrically. The total contraction per mole of sugar, when hydrolysis was complete, varied with the concentration of the catalyst and sucrose. It was concluded that the dilatometric method may be employed with confidence for the investigation of cane sugar hydrolysis in acid solutions, and for the study of invertase action.

The primary salt effect and temperature coefficient for the velocity of hydrolysis of diethylacetal has been studied extensively by Riesch and Kilpatrick.<sup>115</sup> The energy of activation was found to be independent of the salt concentration within the experimental error. It was found that the logarithm of the velocity constant did not vary linearly with the salt concentration, although at high concentrations a linear relationship was approached.

The kinetics of the fourth order reaction,



has been extensively investigated by Bray and Liebhafsky.<sup>8</sup> The electrolyte was mainly perchloric acid in the presence of some sodium bromide and sodium perchlorate. Comparison of the results with those of Young and Bray for the velocity of the reaction,,



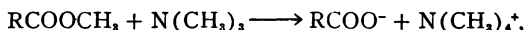
was made. No evidence of specific salt effects was noticed at ionic strengths less than 0.5. The ionization constant of the bisulfate ion, determined from the kinetic data in sulfuric acid and sulfate solutions, was found to be in agreement with the value obtained from conductance and electromotive force measurements.

Infra red absorption was employed by Plyler and Barr<sup>111</sup> to measure the reaction rate of acetic anhydride and water. The error in the determination of the velocity constant is of the order of 10 per cent. The use of the Rayleigh interferometer for the determination of reaction velocities in solution has been discussed by Luten.<sup>88</sup>

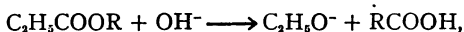
Hammett<sup>45</sup> has brought out several relationships between reaction rates and dissociation constants for reactions of the type,



As an example, we cite the reaction,



in which case the logarithm of the velocity constant was shown to vary approximately linearly with the logarithm of the ionization constant of the acid of the ester. A similar correlation was found for the reaction,

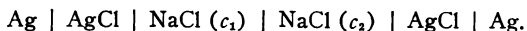


in which case the variation of the logarithm of the velocity constant was linear with the logarithm of the ionization constant of RCOOH. Acid and base catalyses for a number of reactions may be treated successfully in a similar manner. Hammett<sup>46</sup> has also obtained an interesting correlation between a specially defined acidity function, measured in terms of reaction with a series of indicators, and the velocity constants of some reactions catalyzed by strong acids, such as the inversion of cane sugar, the hydrolysis of ethyl acetate, etc.

A number of possibilities for employing isotopes for the purpose of determining mechanisms of reactions which take place in solution, have been pointed out by Wynne-Jones.<sup>154</sup> Applications of these ideas to the neutralization of nitroethane, the mutarotation of glucose, the inversion of sucrose, and the decomposition of nitramide have been discussed.

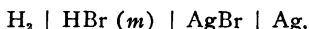
**Thermodynamics of Solutions.** *Electromotive Force and Thermodynamic Properties of Electrolytes.* A very accurate evaluation of the

activity coefficient of sodium chloride at 25°, through the concentration range of 0.005 to 0.1 molal, has been carried out by Brown and MacInnes<sup>10</sup> from measurements of the cells,



The accuracy of their measurements was of the order of 0.01 mv. By combining these results with the transference numbers obtained by Longworth, and the equation of the Debye and Hückel theory containing the mean distance of approach, the activity coefficient of sodium chloride was computed.

Keston<sup>67</sup> has shown that a very reproducible silver-silver bromide electrode can be made from an intimate mixture of 90 percent silver oxide and 10 percent silver bromate made in the form of a paste, which was held on a helix of platinum wire and then heated to 650°. The cells,



were measured from 0.001 *M* to 0.02 *M* at 25°. The electromotive forces were found reproducible to within  $\pm 0.1$  mv., and the results were found to fit the Debye and Hückel equation very closely, if an apparent ionic diameter of 4.5 Ångstroms was employed. Owen<sup>108</sup> by measuring the cells,

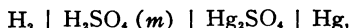


in which X was Cl or I, was able to obtain the standard potential of the silver-silver iodide electrode, relative to the silver-silver chloride electrode, from 5° to 40°. Since the standard potential of the latter is known, he was able to compute the standard potential of the silver-silver iodide electrode through this temperature range. Silver-silver iodide electrodes made electrolytically and by fusion gave identical electromotive forces.

Hamer,<sup>43</sup> and Harned and Hamer<sup>50, 51</sup> have completed a very comprehensive study of the thermodynamics of sulfuric acid in aqueous solutions, the standard electrode potentials of the cells, and reversible electromotive forces of the cells related to the lead accumulator. The standard potential of the cells,



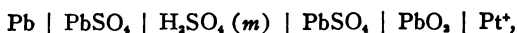
was determined at 5° temperature intervals from 0° to 60°, and at concentrations from 0.0005 to 7 *M*. Two methods of extrapolation were contrasted, and the one which employed the Debye and Hückel theory and the dissociation constant of the bisulfate ion, was considered the better. From these data, and the electromotive forces of the cells,



from 0° to 60° and from 0.05 to 17.5 *M*, Harned and Hamer computed the activity coefficient, relative partial molal heat content, and specific

heat of sulfuric acid in aqueous solution. Since the cell reaction of the first of these cells involves two molecules of water, and the second involves no water, it was possible to compute the activity of water, or the vapor pressure, from the cell measurements. Results obtained by this procedure were in good agreement with the best vapor pressure data at 25°. At 0° the activity coefficient of the acid computed from the electromotive force measurements were in excellent agreement with the freezing point measurements of Randall and Scott. The relative partial heat content at 25°, computed from these results, agrees very closely with the direct measurements of this quantity made by Lange, Monheim and Robinson in the region of concentration of 0.0005 to 0.05 *M*. Values of the relative partial molal heat content and specific heat from 0° to 60° and from 0 to 17.5 *M* were computed.

By combining the electromotive forces of the above cells with those of the cell, Pb (2-phase amalgam) | PbSO<sub>4</sub> | Na<sub>2</sub>SO<sub>4</sub> | Hg<sub>2</sub>SO<sub>4</sub> | Hg<sup>+</sup>, and the cell, Pb | PbSO<sub>4</sub> | Pb<sup>++</sup> | PbSO<sub>4</sub> | Pb (2-phase amalgam),\* obtained by Gerke, Harned and Hamer<sup>51</sup> computed the standard potentials of the electrodes reversible to the sulfate ion, and those related to the electrodes of the lead accumulator. They also obtained the reversible electromotive forces of the cell,

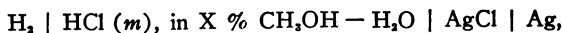


from 0° to 60°, and from 0.05 to 7 *M* sulfuric acid.

Scholl, Hutchison, and Chandlee<sup>122</sup> have measured the cell with hydrogen and mercurous sulfate-mercury electrodes in alcohol solutions containing sulfuric acid. From their results, the standard potential of the cell, and the activity coefficient of the acid from 0.003 to 0.7 *M* have been computed.

The "salt error" and standard potential of the quinhydrone electrode have been the subject of a careful investigation of Hovorka and Dearing.<sup>57</sup> The "salt error" (for fourteen electrolytes) was found to vary nearly linearly with the concentration of solute. La Mer and Armbruster<sup>79</sup> designed a small quinhydrone-silver chloride cell of 2-4 cc. capacity, and found that its electromotive force could be reproduced with an accuracy comparable to that obtainable with a larger cell.

Electromotive forces of the cells,



have been measured from 0° to 40° at 5° intervals, and at hydrochloric acid concentrations from 0.005 to 0.1 *M*, by Harned and Thomas.<sup>53</sup> Two solvent mixtures were employed, containing 10 percent and 20 percent by weight of methyl alcohol, respectively. The standard potentials of the cell were computed.

By employing suitable cells without liquid junction, Harned and Mannweiler<sup>52</sup> have determined the ionic activity coefficient and dis-



sociation of water in sodium chloride solutions. Values of these quantities were obtained over a salt concentration range from 0.02 to 3 *M*, and at temperatures from 0° to 60°. Also, values of the ionic activity coefficient of water in seven chloride and bromide solutions at 25° were compiled from the best available data. It was found that at a given temperature and salt concentration, the logarithm of the ionic concentration product varies nearly linearly with the sum of the reciprocal of the ionic radii obtained from crystallographic data. This shows that greater dissociation of water molecules takes place in the presence of ions of smaller radii.

The thermodynamic properties of mixtures of hydrochloric acid in uniunivalent chloride solutions, and hydrobromic acid in bromide solutions, have been subjected to an analysis by Harned.<sup>48</sup> The results were contrasted with the recent computations of Åkerlöf and Thomas; and it was shown that the two empirical rules suggested by these writers were not valid in the more dilute solutions. In concentrated solutions, the contentions of these authors are more nearly valid, but not strictly so. The results were also discussed in relation to Brønsted's original theory of specific ionic interaction. The deviations from this theory which occur at concentrations from 0.1 to 3 *M* were pointed out. The extended theory of specific interaction as developed by Scatchard and Prentiss may account for these deviations.

Kolthoff and Tomsicek<sup>71</sup> have determined the standard potential of the ferrocyanide-ferricyanide electrode, and its change of the potential in some salt solutions. The variations of the potential with ionic strength in the dilute systems is greater than that predicted by the Debye and Hückel theory.

Valuable contributions to the knowledge of the oxidation potentials of argentous-argentic salts in acid solution have been made by A. A. Noyes, Hoard and Pitzer,<sup>102</sup> A. A. Noyes, Pitzer and Dunn,<sup>104</sup> and A. A. Noyes and Kossiakoff.<sup>108</sup> Although these studies have no direct bearing on the theories of solutions, they are of interest as a contribution to the study of standard electromotive forces and are mentioned in this connection. The oxidation potential of the alkaline permanganate-manganese dioxide electrode has been determined by Andrews and Brown.<sup>3</sup>

Garner, Green, and Yost<sup>29</sup> have measured the electromotive forces of the cells:  $\text{Zn (amal., N}_2\text{)} \mid \text{ZnCl}_2 \cdot 6\text{NH}_3(s) \mid \text{NH}_4\text{Cl (in liquid NH}_3(m)) \mid \text{CdCl}_2 \cdot 6\text{NH}_3(s) \mid \text{Cd (amal., N}_2\text{)}$ . By combining these results with those of cells previously measured by Elliott and Yost, the standard potentials at 25° of the half cells whose reactions are,  $\text{Ti}(s) + \text{Cl}^- = \text{TiCl}(s) + \text{E}^-$ ,  $\text{Zn}(s) + 2\text{Cl}^- + 6\text{NH}_3(l) = \text{ZnCl}_2 \cdot 6\text{NH}_3(s) + 2\text{E}^-$ , and  $\text{Cd}(s) + 2\text{Cl}^- + 6\text{NH}_3(l) = \text{CdCl}_2 \cdot 6\text{NH}_3(s) + 2\text{E}^-$ , have been determined provisionally in liquid ammonia solutions. Provisional values of the activity coefficient of ammonium chloride in liquid ammonia from 1 to 24.4 (*M*) (sat.) have also been obtained.

McBain and Barker<sup>90</sup> computed the activity coefficients of different soap solutions at 90°. The results may be interpreted upon the assumption that, in a given solution, the anion is a polyvalent micelle with its charges spaced far apart. The behavior corresponds to that of a half-weak uniunivalent electrolyte. McBain and Betz<sup>91</sup> estimated the degree of dissociation of straight chain sulfonic acids in aqueous solution from measurements of cells with a liquid junction containing a hydrogen electrode. McBain<sup>89</sup> has compared the degrees of dissociation obtained in this manner with those derived from conductivity and freezing point measurements.

Formal thermodynamic equations for the osmotic and activity coefficients of undissociated, partially dissociated, and completely dissociated solutes, have been stated by van Rysselberghe.<sup>142</sup> In another contribution,<sup>143</sup> this author computed the osmotic and activity coefficients of acetic acid at 0° corresponding to each of these descriptions.

The free energies of reactions involving potassium lead sulfate, lead sulfate, lead iodide, potassium, sodium and lithium ions have been determined at 25°, and at various ion strengths, by Randall and Shaw.<sup>112</sup> The mean activity coefficients of the ions in the equilibrium solutions are about the same as those of barium chloride. One of the solid phases was found to be  $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$ .

A thermodynamic treatment of the theory of electrode potentials has been developed by Gross and Halpern.<sup>40</sup> By considering the electrode processes as proceeding first in the liquid and then in the gas phase, these authors obtained an expression for the normal potential in terms of partly known thermodynamic quantities.

Martin and Newton<sup>99</sup> derived an equation for the electromotive force of a cell with a moving liquid junction. A cell was constructed which contained two silver-silver chloride electrodes in solutions of two different chlorides. A sharp boundary was formed by passing an outside current through the cell. When the electrical flow was interrupted, measurements of the potential were made. The results were not in accord with the equation.

*Activity Coefficients from Vapor Pressure.* Robinson<sup>117, 118</sup> has determined the activity coefficients of the alkali bromides, iodides, nitrates, acetates, and *p*-toluenesulfonates at 25° by measuring the concentrations of these solutions isotonic with known concentrations of potassium chloride solutions. The activity coefficients of bromides and iodides computed from these data are in good accord with electromotive force and freezing point data. Those of the nitrates agree with values computed from freezing point measurements. Dynamic vapor pressure measurements of aqueous solutions of calcium and aluminum nitrates at 25° have been made by Pearce and Blackman.<sup>110</sup> Larsen and Hunt<sup>84</sup> have measured the vapor pressure of solutions of ammonium nitrate, iodide, bromide, and chloride in liquid ammonia solutions. Extrapolation of the results to zero concentration was difficult. The measure-

ments gave a quantity  $k'\gamma$ , and plausible values of  $k'$  were estimated, from which approximate values of  $\gamma$  may be obtained. The results indicate considerable ionic association.

Wynne-Jones<sup>155</sup> has determined the composition of the vapor over known compositions of the mixture  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The mixtures approximate very closely ideal solutions.

The total and partial vapor pressures of mixtures of ethyl alcohol and cyclohexanol at  $25^\circ$  have been measured by Washburn and Handorf,<sup>147</sup> and the activity coefficients of the components of the mixtures have been evaluated. The deviations from ideal behavior have been interpreted on the basis of the differences in polarity and internal pressure of the components.

**Solubility.** Hildebrand<sup>54</sup> reported a series of experimental tests of his general equation for the calculation of solubility from the properties of the pure solvent and solute. To make the tests as general and vigorous as possible, he selected solutes which would lead to unusually large deviations from ideality, and both polar and non-polar solvents were used. In view of the approximations involved in the derivation of the equation, the agreement with experiment is remarkable. It was shown that departures from spherical symmetry in the molecules, and the presence of dipole moments do not necessarily vitiate the calculations. Indeed, even the *liquid-liquid* system  $n\text{-C}_{32}\text{H}_{66}\text{--SnI}_4$  can be treated with reasonable success. Guggenheim\* has criticized the application of Hildebrand's equation, based upon the assumption of perfectly random distribution, to solutions deviating so widely from ideality as to be only partially miscible. He proposed a general statistical treatment of his own, but it predicts more serious consequences for departures from random distribution than those observed. Furthermore, Scatchard and Hamer,<sup>120</sup> in an extensive investigation of liquid-liquid systems, found Guggenheim's treatment less satisfactory than their simpler theoretical deductions.

Several important papers appeared on the thermodynamics of solid solutions. Seltz<sup>124</sup> developed methods for determining the forms of the liquidus and solidus curves for binary systems, showing complete solid miscibility, where the deviations from Raoult's law are known for the liquid and solid solutions. Scatchard and Hamer<sup>121</sup> applied equations for the chemical potentials to such systems, and developed general relations which they employed in a successful analysis of the experimental data on the Ag-Pd, and Au-Pt systems. Seltz<sup>125</sup> developed equations for calculating the solidus and liquidus surfaces, with tie lines, for ternary systems composed of perfect liquid and solid solutions. Thompson<sup>136</sup> made a study of the solubility of lead in mercury throughout the temperature range  $20^\circ$  to  $70^\circ$ .

Several studies of the solubility of gases under high pressure have been reported. Wiebe and Gaddy<sup>148</sup> measured the solubility of a 3:1

\*Guggenheim, E. A., *Proc. Roy. Soc. (London)*, **A148**: 304 (1935).

mixture of  $H_2$  and  $N_2$  at  $25^\circ$  and of He at 0, 25, 50, and  $75^\circ$ .<sup>149</sup> The pressure range extended to 1,000 atmospheres. The solubility of He passes through a minimum at about  $30^\circ$ . The solubilities of helium and argon in numerous salt solutions at  $25^\circ$  were determined by Åkerlöf.<sup>1</sup> The data could be described by the ordinary "salting out" relation,  $\log S = \log S_0 - k m$ , in which  $S_0$  and  $S$  are the solubilities in pure water and in  $m$ -molal salt solution. The salting out constants,  $k$ , were found to have the same order of magnitude as those of other non-electrolytes. This conclusion was based upon an extensive summary of salting out studies for gaseous, liquid, and simple solid non-electrolytes appearing in the literature. The salting out coefficients of a complicated compound such as hemoglobin<sup>36</sup> is considerably higher than those considered here. The peculiar specific nature of the salting out constants was emphasized, however, and it was pointed out that the magnitudes of these constants do not arrange themselves in the order of the activity coefficients, or mean atomic radii of the electrolytes present.

Åkerlöf and Turck<sup>2</sup> determined the solubilities of a number of strong, highly soluble salts in methanol-water mixtures, and in hydrogen peroxide-water mixtures at  $25^\circ$ . The results in the methanol-water solutions showed a steady decrease in the logarithm of the solubility with mole fraction of methanol. The distribution of the plots of these variables was paralleled by plots of the data for similar salt-organic solvent-water systems available in the literature. It was pointed out, as a rough approximation, that the ratio of the slopes of these plots (for small organic solvent concentration) for a given pair of salts was independent of the organic solvent; and for a given pair of organic solvents, the ratio was independent of the salt. In the latter case, the numerical value of the ratio is of the order of magnitude of the ratio of the corresponding slopes for the dielectric polarization curves of the solvent mixtures.

In hydrogen peroxide-water mixtures the solubility relationships of the various salts were highly specific. Sodium chloride and nitrate were salted-out, and potassium chloride and nitrate and sodium fluoride were salted-in by hydrogen peroxide, and the effects were very pronounced. In the case of sodium chloride and nitrate (and also lead nitrate) this effect is contrary to what might be expected from consideration of the very high dielectric constants of pure hydrogen peroxide-water mixtures. This interesting situation is further complicated by the distribution experiments of Gorin,<sup>35</sup> from which it was shown that *all* of the above salts behaved similarly in salting-in hydrogen peroxide. In one respect, however, Gorin's results also point to a peculiarity of sodium salts, since it was found that with the exception of sodium ions the order of the salting-in effects of the ions on hydrogen peroxide followed the same order as the salting-out effect on other non-electrolytes in general. The salting-out of allyl alcohol from water solution by a wide variety of salts was investigated by Ginnings and

Dees.<sup>33</sup> They expressed their results satisfactorily by means of equations of the form,

$$y = a + b(10)^{-cx},$$

in which  $a$ ,  $b$ , and  $c$  are empirical constants, and  $x$  and  $y$  are the percentages, by weight, of salt and alcohol, respectively. The salting-out of butyl alcohol by various amino acids was found<sup>21</sup> to decrease with increasing length of the hydrocarbon chain and to decrease with increasing concentration of the amino acid.

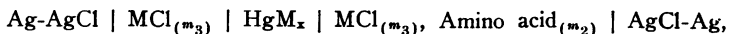
Brown and MacInnes<sup>11</sup> described an electrometric titration method by which they determined the solubility of silver chloride in a dilute potassium nitrate solution. They included a theoretical discussion of the liquid junction and volume corrections, and of their novel method of carrying out the computations. By virtue of the high sensitivity of the method, they were able to observe a small but unmistakable decrease in solubility with time (about 0.06 percent per hour).

Several papers appeared on solubilities in non-aqueous solutions of electrolytes. Swearingen and Florence<sup>134</sup> measured the solubility of sodium bromide in acetone solutions of lithium and calcium perchlorates. The activity coefficient of sodium bromide was found to be considerably lower than required by the Debye-Hückel theory, although the concentrations involved were probably too high to expect good agreement. A similar result was obtained by Davidson and Griswold<sup>18</sup> for zinc acetate in glacial acetic acid solution of sodium and ammonium acetates. In this case, however, it was possible to show, by comparison with barium acetate under the same circumstances, that a part of the observed departure could be attributed to the amphoteric nature of zinc acetate.

The solubilities of various amino acids have been reported in water,<sup>138</sup> and in alcohol-water mixtures.<sup>157</sup> McMeekin, Cohn, and Weare<sup>97</sup> made an extensive study of the solubility of amino acid derivatives for comparison with previously reported values for the corresponding free acids. It was found that the ratio of the solubility in alcohol to that in water is increased approximately threefold for each terminal  $\text{CH}_2$  group in the molecule. This rule applies both to amino acids and to their derivatives. On the other hand, a  $\text{CH}_2$  group situated between strongly polar groups, as in aspartic acid and asparagine, does not measurably affect the solubility ratio. The solubilities of the amino acid derivatives increased with alcohol content of the mixtures, which is contrary to the salt-like behavior of the free acids. An estimate of the effect of zwitterionic structure upon solubility ratio was obtained by a comparison of the data for hydantoic acid with asparagine, and with glutamine. The values obtained are in excellent agreement. In a review of the chemistry of proteins and amino acids, Cohn<sup>15</sup> has emphasized the importance of such comparisons in the study of the spatial relationships in amino acid molecules. Cohn's review includes extensive discussions of dimensions, dielectric properties, and salting-

out effects of amino acids, and goes into considerable detail concerning applications of the equations of Scatchard and Kirkwood.

Joseph<sup>63</sup> reported an interesting potentiometric investigation of the mutual interaction of amino acids and salts. The measurements were made with amalgam double cells of the type,



in which M represents Na, Tl, or Zn. The influence of amino acids upon the salts is such that  $\log (\gamma_3/\gamma_3^\circ)$  increases linearly with  $m_2$  at high salt concentrations, and that the slope is independent of  $m_3$ . Accordingly, the corresponding function  $\log (\gamma_2/\gamma_2^\circ)$  increases linearly with  $m_3$ , and the slope is independent of  $m_2$ . These slopes are in agreement with salting-out coefficients derived from solubility measurements. It was pointed out that in aqueous solutions the salting-out effects are significant even at low concentrations, because both the salting-out and electrostatic forces appear to be approximately proportional to the first power of the concentration. The interaction observed between glycine and zinc chloride was shown to be closely paralleled by the results of freezing point on glycine with other (2-1) valence type salts.

*Calorimetric Measurements.* An extensive calorimetric study of amino acids was reported by Zittle and Schmidt.<sup>157</sup> They measured heats of dilutions for solutions of eighteen amino acids, and found much larger differences than would be anticipated from considerations of molecular structure. Thus the variation of the relative apparent molal heat contents of *d*-arginine and *d*-lysine with concentration are large, but of *opposite* sign. Heats of solution were calculated and compared with values derived from solubility data. The heat capacities of glycine, *dl*-alanine, and *dl*-valine were found to be always positive, and their variation with concentration linear in *m*. This supports the theoretical predictions of Scatchard and Kirkwood. Partial molal volumes were also positive, but varied only slightly with concentration.

Edsall<sup>19</sup> showed qualitatively how the formation of zwitterions might influence apparent molal heat capacities. The heat capacities of aqueous solutions of various hydrazonium salts and their heats of solution were measured by Cobb and Gilbert.<sup>14, 32</sup>

Gucker and Rubin<sup>41</sup> calculated the apparent isochoric heat capacities,  $\Phi(C_{v2})$ , for six (1-1) electrolytes, and found that their variation with  $\sqrt{c}$  was approximately linear, but exhibited the same degree of individuality as the corresponding isopiestic quantities,  $\Phi(C_{p2})$ . Since the absence of the expansion term simplifies the theoretical interpretation in the isochoric system, the persistence of marked individuality at low concentrations is particularly striking. The difference between the isopiestic and isochoric apparent molal heat capacities varied little with concentration, and was of the order of 3 to 11 cal. depending upon the salt. The values of  $\Phi(C_{v2})$  are the more negative.

In continuing his interesting series of papers on the non-comparative criteria of the purity of organic compounds, Skau<sup>127</sup> discussed some of the limitations of the application of specific heat data to the determination of purity.

*Ionization Constants.* The use of ultraviolet spectrophotometry in the determination of ionization constants was investigated by Flexser, Hammett and Dingwall.<sup>25</sup> The validity of the method was indicated by measurements on benzoic acid, aniline, and 2,4-dinitrophenol, and it was then applied to a series of very weak bases in sulfuric acid solutions.

Wooten and Hammett<sup>153</sup> measured the difference in the relative ionization constants (referred to benzoic acid) of 33 carboxylic and phenolic acids in water, and in butyl alcohol. In general, their results were more readily interpreted according to a paper by Schwarzenbach and Egli than by the familiar Born equation, but the data on *ortho*- or  $\alpha$ -substituted acids were not satisfactorily accounted for in either case. Jukes and Schmidt<sup>64</sup> determined the apparent ionization constants of ten fatty acids in ethanol-water mixtures at 20°.

La Mer and Korman<sup>82</sup> found that the acidic ionization constant of deuterioquinone is 3.84 times as great as that for hydroquinone. This is in accord with known behavior of weak acids, and has been interpreted by Halpern<sup>42</sup> in terms of the difference in zero-point energy of the proton or deuteron when attached to a water molecule, or to an acid radical.

Kolthoff and Tomsicek<sup>72</sup> evaluated the fourth ionization constant of ferrocyanic acid ( $K_4 = 5.6 \times 10^{-5}$  at 25°). The method used was unusual, and was based upon the effect of hydrogen ions upon the potential of the ferro-ferricyanide electrode.

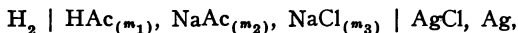
The classical dissociation constant of benzoic acid at 25° was determined by Riesch and Kilpatrick<sup>116</sup> in nine aqueous uniunivalent salt solutions. From these results and available values of the salting-out coefficient for molecular benzoic acid, the corresponding mean activity coefficients of the ionized acid were calculated. A concordant redetermination of the thermodynamic ionization constant of boric acid<sup>108</sup> at various temperatures has been reported. The thermodynamic ionization constants of carbonic acid were determined by MacInnes and Belcher<sup>96</sup> at 38° by means of the glass electrode. The values,  $K_1 = 4.91 \times 10^{-7}$  and  $K_2 = 6.25 \times 10^{-11}$ , were obtained, but the value of  $K_1 (= 4.82 \times 10^{-7})$ , determined conductometrically,<sup>126</sup> is recommended for adoption.

The apparent ionization constants of some dihalogenated tyrosine compounds were determined at 25° and 40° by Winnek and Schmidt.<sup>65</sup> The solubility method was employed. Tomiyama<sup>137</sup> reported values for canaline and canavanine.

Greenstein and Joseph<sup>38</sup> determined the apparent ionization constants of  $\alpha$ -aminotricarballylic acid and glycyl- $\alpha$ -aminotricarballylic acid electrometrically at 25°. They estimated the thermodynamic con-

stants. Kumler and Daniels<sup>77</sup> determined the apparent dissociation constants of *L*-ascorbic acid in water, and of diethyl dihydroxymaleate in water, and alcohol-water solutions.

The thermodynamic ionization constant of acetic acid was determined in 10 percent and 20 percent methanol solutions by Harned and Embree.<sup>49</sup> They employed cells of the type,



and carried out the measurements at 0, 10, 20, 25, 30, and 40°. This is apparently the first time that cells without liquid junctions have been employed in an extensive study of a weak acid in solvents other than water. The temperature variation of the ionization constants could be expressed by the empirical equation,

$$\log K = \log K_m - 5 \times 10^{-5} (t - \theta)^2,$$

in which  $\theta$  is the temperature of the maximum value  $K_m$ . In this case the equation expressed the data to better than 1.5 percent, and this is the order of the concordance usually obtained for acids in water. The well-known dangers inherent in the use of such an empirical equation for the estimation of *derived* quantities ( $\Delta C_p$ , for the ionization process, for example) has been emphasized by Walde.<sup>144</sup> The effect of the alcohol upon the strength of the acid could be expressed by the linear dependence of  $\log K$  upon  $1/D$  as a first approximation.

Goodhue and Hixon<sup>34</sup> determined the apparent ionization constants of five bases and five acids in pure ethanol by the use of the hydrogen and  $\text{Hg-HgI}_2$  electrodes. Agreement with conductance values reported by Goldschmidt was satisfactory in view of the magnitude of the liquid junction potentials. It was shown that the results were in harmony with Brönsted's generalized interpretation of acids and bases.

Concerning subjects closely connected with the determination of ionization constants, we might mention papers dealing with *pH* determination. Kilpatrick<sup>68</sup> reviewed the colorimetric method and Atkin and Thompson<sup>4</sup> outlined a variety of methods. Kolthoff<sup>70</sup> discussed the mechanism of the ionization of acids and bases, and its statistical interpretation at "absurdly" low concentrations. The effect of ionic strength upon protein ionization was investigated by Smith<sup>128</sup> who found that the *pH* of the apparent isoelectric point of egg albumin varied linearly with both the ionic strength, and the concentration of the albumin itself. These relationships were employed to determine the "true" isoelectric point at zero ionic strength and protein concentration.

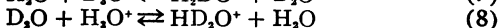
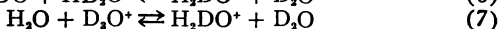
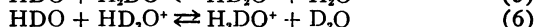
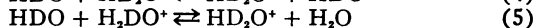
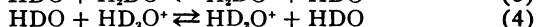
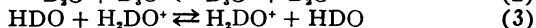
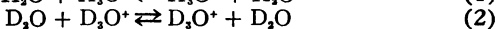
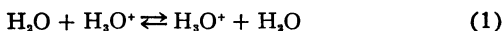
*Compressibility.* Gibson<sup>30</sup> published an important paper on the concentration-compressibility relationships in solutions of electrolytes. His conclusions were based on measurements of the compressions to 1,000 bars of solutions of sixteen salts, and acetic acid over the whole concentration range at 25°. It was shown that the apparent com-



pression of the salts varied linearly with the square root of the volume concentration within the experimental error. By means of a plot of the bulk compressions of solutions of twenty-four salts against the "modified ionic strength" [ $\frac{1}{2}c(v_+z_+ + v_-z_-^2)$ ], note that the valence of the cation is raised to the first power only] it was found possible empirically to estimate the bulk compression of any solution, with an error less than  $\pm 10$  percent from a knowledge of the concentration and the nature of the solute. On the assumption of Tammann's hypothesis, that water in aqueous solutions behaves like water under a pressure greater than the external pressure, the "effective pressure" which a salt exerts upon the solvent could be calculated from the data. In all cases this "effective pressure" was directly proportional to the product of the volume concentrations of salt and water. The linear relationship between the concentration, and the apparent molal compression of solutions of acetic acid is similar to that of solutions of strong electrolytes. Gucker has previously observed similar behavior in sugar solutions. In a later paper Gibson<sup>31</sup> reported the results of his measurements of the compressions and specific volumes of aqueous solutions of methanol and resorcinol at 25°. The apparent compression of resorcinol varied linearly with the square root of the concentration, but the apparent volumes of resorcinol and the apparent volumes and compressions of methanol were definitely not linear in  $\sqrt{c}$ . Although the square root relation is predictable for strong electrolytes by differentiation of the Debye-Hückel equation, the behavior of certain non-electrolytes reported above shows that important forces besides those of interionic attraction are involved.

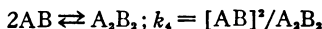
Scott and Bridger<sup>123</sup> observed pronounced departures from the usual square root relationship between concentration and apparent molal volumes, or apparent molal compressibilities, in concentrated solutions of lithium chloride and bromide. Distinct discontinuities in the curves of these variables were obtained, and several of these were reported for the first time. The authors suggested that the results are more readily interpreted in terms of variation in distribution of solute ions than in the number of layers of water molecules involved in hydration of the ions. Bridgman and Dow<sup>9</sup> determined the compressibilities of aqueous solutions of glycine,  $\alpha$ -aminobutyric acid, and  $\epsilon$ -aminocaproic acid at 25 and 75°. Their results presented some very interesting anomalies. The apparent molal volumes are neither linear in  $\sqrt{c}$ , as required by Debye-Hückel theory for ordinary ions, or linear in  $c$ , as required by Scatchard and Kirkwood's equations for zwitterions. The initial slopes of the curves obtained by plotting apparent molal volumes against pressure are all negative. This requires that the apparent molal compressibilities of the amino acids are positive. This is contrary to the behavior of all other electrolytes, and also to the behavior of urea, which, in common with the amino acids, increases the dielectric constant of aqueous solutions.

**Conductance and Transference.** Although the conductance of aqueous solutions of strong electrolytes has received scant attention this year, a very interesting study of conductance in water-deuterium mixtures has been made. Baker and La Mer<sup>5</sup> found that the conductance of 0.01 *N* potassium chloride in H<sub>2</sub>O—D<sub>2</sub>O mixtures is very nearly linear in the mole fraction of deuterium oxide, and more than 90 percent of the decrease in conductance can be accounted for by the viscosities of the mixtures. In the case of 0.01 *N* hydrochloric acid, the decrease in conductance exhibited a pronounced departure from linearity, with a well-defined maximum departure (6.5 percent of  $\Delta$ ) in the 1 to 1 mixture. According to the generally accepted view, the high conductance of the H-ion is attributed to a series of proton exchanges, which in H<sub>2</sub>O—D<sub>2</sub>O mixtures may take the following forms:



The exchanges represented in equations 1 to 4 are symmetrical, and are accompanied by no change in energy, but the remaining exchanges can only occur with absorption or evolution of heat to the surrounding medium. The necessity for this interchange of energy will tend to decrease the frequency with which the latter types of exchanges take place. Since in 50 percent deuterium oxide we have the maximum probability that an acid ion will be in the immediate neighborhood of water molecules to which it cannot readily transfer its proton, we should expect a lower conductance than that calculated according to the additivity law (linear variation with D<sub>2</sub>O). This effect had been qualitatively predicted by Halpern.

Concerning conductance in media of low dielectric constants, and the general question of the association of ions in solution, Fuoss<sup>26</sup> and Kraus<sup>73</sup> have contributed reviews of their most recent work. Together<sup>28</sup> they examined the conditions under which ion pairs might associate into quadrupoles:



The numerical value of  $k_4$  was calculated for tri-isoamylammonium picrate in benzene solutions from freezing point data. Considering the quadrupole as an ellipsoid (of axis  $a$  and  $\lambda a$ ) containing a point dipole of strength  $\mu$  at its center, and parallel to the major axis, they derived the equation,

$$k_4^{-1} = \frac{N}{2000} \left( \frac{\pi}{3} \right)^{3/2} \frac{\mu^2}{Dkt} \frac{e^2}{y^{7/2}} (-1 + \frac{1}{2} \lambda^2)^{-1},$$

where  $y = \mu^2 / \lambda^3 a^3 D k T$ . From the value of  $k_4$  derived for the above salt, this leads to the physically reasonable value,  $\lambda a = 5.54 \times 10^{-8}$  cm.

Cox, Kraus and Fuoss<sup>17</sup> determined the conductance of several tetrabutylammonium salts in anisole ( $D=4.29$ ), ethylene bromide ( $D=4.76$ ), and ethylene chloride ( $D=10.23$ ) at 25°. Their results can be qualitatively interpreted in terms of association into ion pairs and triple ions in accordance with earlier papers by Fuoss and Kraus, and the  $a$ -parameters (distances between charges) derived from their equations are of the order of 5 or 6 Angstrom units. This paper is of considerable technical interest in that, at concentrations between  $10^{-5}$  and  $10^{-6}$   $N$ , the conductances were reproducible to 0.1 to 0.2 percent, and allowed a very accurate determination of the influence of adsorption of electrolyte upon the electrodes. The amount of adsorbed electrolyte (tetrabutylammonium picrate in ethylene chloride) was, within the experimental error, independent of the concentration, and corresponded to a monomolecular layer on the surface of the electrodes.

Jones and Christian<sup>60</sup> made a careful study of galvanic polarization by alternating current in conductance cells, and found it independent of electrode separation and current density, and not very sensitive to temperature, or the nature of the electrolyte. It was, however, greatly influenced by the composition of the electrodes. Polarization capacitance decreases with increasing frequencies, and polarization resistance is inversely proportional to the square root of the frequency. This latter relation was proposed by Jones and Bollinger<sup>50</sup> as a means of testing the quality and sufficiency of electrode platinization, and of calculating the true resistance, free from polarization effects.

Fuoss<sup>27</sup> tabulated values of the function,  $F(z)$ , for the rapid calculation of the degree of ionization of binary electrolytes from conductivity measurements. The equation is

$$\alpha = \frac{\Lambda}{\Lambda^\circ F(z)}.$$

The conductance concentration curves obtained by McBain and Betz<sup>92</sup> with simple straight chain sulfonic acids exhibit several inflections, with pronounced minima at about  $N/20$ . The possibility of association of like ions to form ionic micelles was considered. Freezing point data were also brought to bear on this question.<sup>93</sup>

The conductance of saturated solutions of some slightly soluble substances have been determined by Johnson and Hulett,<sup>58</sup> and the values obtained were proposed for the convenient determination of cell constants. They also studied sodium and potassium chlorides at 0° and 25°. Campbell and Cook<sup>12</sup> made a conductometric investigation of the precipitation of strontium sulfate from its supersaturated solutions.

Conductivities of aqueous solution of glycine, *dl*-valine and *l*-asparagine were determined by Mehl and Schmidt,<sup>100</sup> and these and other data on amino acids were compared with theoretical predictions. The agreement is only approximate. Bent and Dorfman<sup>7</sup> interpreted their

conductance data on sodium triphenylboron and disodium tri- $\alpha$ -naphthylboron in ether as showing that the sodium atoms in the latter salt ionize simultaneously by virtue of a rearrangement of valence electrons in the molecule.

From new measurements of the conductance of potassium bicarbonate and carbonic acid solutions at 25°, and of the relative conductances of saturated carbon dioxide solutions, and of potassium bicarbonate, potassium chloride, and hydrochloric acid (0.001 *N*) at other temperatures, Shedlovsky and MacInnes<sup>126</sup> calculated the first ionization constant of carbonic acid from 0 to 38°. Their values are considered more reliable than those previously determined electrometrically.

Greenberg and Larson<sup>87</sup> measured the conductivities of solutions of casein, edestin, and gelatine in anhydrous lactic, acetic, and formic acids. In the first two solvents, the conductivities were very low, but in formic acid solutions, the conductance of the proteins were comparable to those of alkali formates, indicating the formation of well defined, ionizable salts with formic acid. Some Hittorf numbers were also determined.

McBain and Foster<sup>95</sup> reported new measurements of surface conductivity exhibited by potassium chloride solutions in contact with glass surfaces, and by films of fatty acids at the air-water interface. Several interpretations are discussed. Urban, White and Strassner<sup>141</sup> developed equations, based on the Stern double layer, for calculating specific surface conductivities, and the thickness of the diffuse (Gouy) layer. The authors' experimental measurements of specific surface conductivity in potassium chloride solutions are in accord with their equations, but not with Gouy's theory. The numerical magnitude of their values is less than that of data obtained by McBain and co-workers. Urban, Feldman, and White<sup>140</sup> showed that specific surface conductivity measured with alternating current is higher than with direct current.

Longsworth<sup>86</sup> continued his careful moving boundary measurements to include five more 1-1 electrolytes, and calcium chloride and sodium sulfate. At the lowest concentrations studied (0.01 *N*) the results for the unsymmetrical salts did not approach the theoretical limiting tangents, for which the slope should be about  $\sqrt{2}$  times greater than that observed for calcium chloride, and of opposite sign from that found for sodium sulfate. Among the 1-1 electrolytes, only potassium nitrate exhibited a persistent departure (more positive) from the theoretical slope, and in this respect paralleled the previously reported behavior of silver nitrate. No quantitative explanation of these "anomalous" results has yet been advanced, but it is usually assumed that they are due to ionic association. A summary of the moving boundary data from the same laboratory shows that all of the other 1-1 electrolytes studied approach the theoretical slopes at high dilution, and their regular departures at higher concentrations conform to the semi-empirical equation previously proposed by Longsworth. Owen<sup>109</sup> found that the characteristic arbitrary parameter of this equation could be approxi-

mated in terms of the limiting slope. This leads to a more general, though less accurate, equation by which it is possible to estimate certain transference numbers in dilute solutions from limiting ionic conductances alone. The assumption, that the "normal" behavior of the *free ions* of potassium and silver nitrates is represented by such a general equation, might lead to some semi-quantitative explanation of the departure of these salts from the theoretical slopes.

Longworth<sup>85</sup> determined the mobility of the hydrogen ion constituent in aqueous mixtures of hydrochloric acid and calcium chloride at a constant total concentration of 0.1 *N*. The observed decrease in hydrogen ion mobility is only 44.1 percent of the value predicted theoretically. Such a discrepancy is not unexpected at 0.1 *N*, but it is surprising that this figure is almost identical to that previously obtained (44.2 percent) in hydrochloric acid-potassium chloride mixtures at the same concentration.

Hamer<sup>44</sup> completed a very comprehensive electromotive force study of the transference number of the hydrogen ion in aqueous sulfuric acid solution. The concentration range varied from 0.05 to 17 molal, and the values at 0 concentration were estimated by extrapolation. Measurements were made at 0, 10, 15, 25, 35, 45 and 60°.

**Diffusion.** Two valuable contributions have appeared from the Rockefeller Institute for Medical Research on the theory of diffusion in cell models. Longworth<sup>87</sup> has extended his theory\* to the case of the simultaneous diffusion of two electrolytes and water. A solution of the equations has been obtained for the steady state. A general solution which would include the time curve has not been obtained. Favorable comparison has been obtained between the theory and the experiments on ion distribution in living cells performed by Osterhout, Kamerling, and Stanley. Teorell<sup>135</sup> has deduced equations for an interesting case. Electrolytes are on both sides of the membrane, and one of them is assumed to diffuse. The concentration and electrical potential gradients set up by this diffusion cause a redistribution of all the ions. By employing the method of treatment of Nernst and Planck, equations for the steady state were developed. It was shown that very marked differences in concentrations of the ions on the two sides of membrane were to be expected, and the suggestion was made that such considerations may explain some of the large concentration differences occurring in biological systems.

Eversole and Doughty<sup>22</sup> have deduced equations for the diffusion coefficient of both charged and uncharged particles as a function of the distance of penetration into a medium, such as a gel. Concentration-distance curves for this undisturbed diffusion are given. Preliminary colorimetric measurements of the diffusion of cupric chloride into gels indicate that the equations are useful.

McBain and Dawson<sup>94</sup> employed a diffusion cell with a sintered

\*Longworth, L. G., *J. Gen. Physiol.*, 17: 211 (1933).

glass membrane to measure the differential and integral diffusion coefficients of potassium chloride at 25°, and at concentrations from 0.1 to 2 *N*. This method is rapid and simple, and the results indicate that it is among the most precise for the determination of diffusion data.

**Viscosity.** The theoretical predictions of the interionic attraction theory applied to viscosity have been subjected to a careful experimental test by Jones and Fornwalt.<sup>61</sup> They measured the relative viscosities of solutions of potassium chloride, bromide, and iodide, and ammonium chloride at 25° in absolute methanol down to concentrations as low as 25 to 50 × 10<sup>-5</sup> *N*. It was found that the general equation of Onsager and Fuoss,

$$\eta = 1 + Ac^{\frac{1}{2}} + Bc + Dc \log c,$$

represents the data up to 0.35 *N*, with an average deviation less than ±0.01 percent. A comparison of the experimental and theoretical values of the limiting slope, *A*, brought out discrepancies of about the order of the differences obtained by curve-fitting over the *entire* concentration range, or at high dilution only. In the latter case the logarithmic term was not included. Although the propriety of testing the theory quantitatively by the inclusion of data at concentrations outside of the "high dilution" range may be open to question, it seems quite proper to interpret the agreement obtained as indicative of the essential validity of the theory.

The viscosities and densities of concentrated solutions of pure sodium and potassium carbonates and hydroxides, and of their mixtures, have been reported.<sup>56</sup>

**Surface Tension.** Jones and Ray<sup>62</sup> published an important note on an experimental study of the surface tensions of very dilute salt solutions. They found that the relative surface tensions of the electrolyte solutions studied (potassium chloride, cesium nitrate, and potassium sulfate), were slightly *less* than unity at high dilution (*C* < 0.006 *N* for potassium chloride), and increasingly greater than unity at higher concentrations. This initial *decrease* in surface tension is contrary to the theoretical predictions of Wagner and of Onsager and Samaras. Measurements on 0.0005 to 0.005 molar sugar solutions with the same apparatus showed only an increase in surface tension.

Surface tension measurements have been applied to a kinetic study of ester hydrolysis,<sup>47</sup> and a simple device described for carrying out measurements upon very small samples.<sup>101</sup> Washburn and Berry<sup>146</sup> applied the capillary rise surface tension method to the estimation of the dimensions of the sodium palmitate molecule. Their results are of the same order of magnitude as similar quantities measured by the Langmuir film method. Cassel<sup>13</sup> pointed out objections to the theory underlying the calculations of these authors.

Some important physical properties of methanol-chloroform

mixtures were measured by Conrad and Hall.<sup>16</sup> Although the vapor pressure and viscosity of these mixtures are quite abnormal, the surface tension, compressibility, density, and index of refraction were found to be ideal functions of the composition.

**Dielectric Constants.** Greenstein, Wyman, and Cohn<sup>39</sup> investigated the dielectric constants of solutions of the tetrapoles diaminodithiodicaproic acid and lysylglutamic acid. The increase in dielectric constant with concentration is linear, and especially large in the case of lysylglutamic acid. The data were interpreted in terms of a twisting of the hydrocarbon chains due to electrostatic forces between the charged amino and carboxyl groups. Measurements of this sort can be expected to shed some light upon the very obscure question of the spatial configuration of proteins.

Because of their solubility in solvents of either high or low dielectric constants, and their ability to retain their zwitterion structure in nearly all solvents, the betaines and a closely related substance, *N*-dimethylantranilic acid, offer interesting possibilities for dielectric investigations. Edsall and Wyman<sup>20</sup> made a very extensive study of the dielectric constants (and apparent molal volumes) of dilute solutions of *o*-, *m*-, and *p*-benzbetaine, pyridinebetaine, betaine, and *N*-dimethylantranilic acid and its methyl ester. The solvents employed were water, ethanol, and benzene, and various water-ethanol and ethanol-benzene mixtures selected to give a representative range in dielectric constants. Because of the relative rigidity of the benzene ring in the benzbetaines (compared to straight chain amino acids) it was possible to estimate polarizations with some certainty from models based on x-ray and electron diffraction data. The authors' calculations indicated that the volume polarizations derived from Wyman's equation,  $p = (D-1)/3$ , are about 20 percent higher, but closely *proportional* to the true values. The dielectric data were expressed numerically as  $\delta$  from the limiting linear relation,  $D = D_0 + \delta c$ . In solvents of low  $D$ , it was found that  $\delta$ -values for the betaines are much lower than in water. Reasons were advanced for interpreting this fact in terms of molecular deformation rather than association. The dipole moment of *N*-dimethylantranilic acid in benzene is about three times as great as that of its methyl ester, indicating that the acid retains its zwitterion structure even in benzene. Electrostriction of the solvent due to the betaines decreases with increasing dielectric constant of the solvent, and the magnitude of the observed effects is in accord with theory.

Kumler<sup>76</sup> pointed out that the current designation of association as the cause of the variation of molecular polarization ( $p_2$ ) of polar liquids (in non-polar solvents) with concentration can be only partially correct. He showed that a large part of the variation is accounted for by the form of the Debye equation, which sets the limit,  $p_2 = \text{molal volume}$ , if  $D$  is increased without limit.

Wilson and Wenzke<sup>152</sup> measured the electric moments of a number of acetylenic acids. The values for propiolic, tetrolic, and phenylpropiolic acids are about 25 percent higher than those of acetic, propionic, and phenylacetic acids. Since the presence of the triple bonds is also accompanied by about a hundred-fold increase in ionization constant, the hydrogen of the carboxyl group undoubtedly becomes more positive in character in the presence of the triple bond.

Svirbely, Ablard and Warner<sup>181</sup> measured the densities and dielectric constants of solutions of *d*-pinene, *d*-limonene, methyl benzoate and ethyl benzoate in benzene. Because these properties were not linear with mole fraction of solute at high dilution, the molar polarization at infinite dilutions were obtained by graphical extrapolation. The values so obtained were subsequently checked by Otto,<sup>105</sup> who performed the extrapolation according to Hedestrand's formula. Otto also determined the moments for solutions of various alkyl esters and derivatives of boric acid in benzene and dioxane. Approximate equality of the values in the two solvents indicated absence of association and compound formation. Otto and Wenzke<sup>107</sup> measured the dielectric constants of solutions of phenylethylene and some of its simple derivatives in benzene at 25°. Phenylethylene was found to possess a small electric moment opposite in direction to that of toluene.

Svirbely and Warner<sup>183</sup> discovered an empirical relation between electric moment and directive influence for substitutions in the benzene ring. They showed that if the electric moment of a mono-substituted benzene derivative is greater than  $\sim 2.07 \times 10^{-18}$  e.s.u., the next substituted group will be directed to the *meta*-position, but if the moment is less than  $\sim 2.07 \times 10^{-18}$  e.s.u., the next group will be directed to the *ortho*- and *para*-positions. Changes in the directive influence with concentration, solvent, temperature, etc., are anticipated by alteration in electric moment with these variables.

The electric moments of a number of acetylenic halides and alcohols were determined by Toussaint and Wenzke.<sup>189</sup> The moments of the halides were influenced by the position of the triple bond. Otto<sup>106</sup> measured the dielectric constants of solutions of several dialkoxyalkanes in benzene at 25°. The independence of the calculated electric moments of the nature of the alkyl group was submitted as evidence of constancy in the valence angle between the two alkoxy groups. Williams<sup>150, 151</sup> reviewed the chemical applications of recent dielectric constant theory and measurements, and included an extensive bibliography.

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## Chapter II.

# The Kinetics of Homogeneous Gas Reactions.

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**Organic Decompositions.** A number of studies have appeared this year which indicate the importance of molecular fragments in many forms of chemical reactions. The mechanism of the methane decomposition is still under consideration and Kassel<sup>23</sup> has affirmed his belief in the primary decomposition into  $\text{CH}_2 + \text{H}_2$ , as opposed to the primary reaction  $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$  proposed by Rice and Dooley.\* Belchetz and Rideal,<sup>3</sup> from experiments on the decomposition of methane on carbon filaments, agree with the former mechanism of dissociation into methylene radicals and hydrogen. The reaction of deuterium atoms produced by excited mercury has recently been studied<sup>79</sup> and shown to proceed at temperatures as low as  $40^\circ \text{C}$ ., indicating a value of very approximately 5 calories for the reaction  $\text{D} + \text{CH}_4$ , in contrast with the value of 17 calories obtained by Geib and Harteck.<sup>†</sup> The exchange reaction<sup>39</sup> between deuterium and methane occurs readily on catalytic surfaces above  $184^\circ \text{C}$ . Preliminary results on the rate of combination of deuterium and ethylene have been reported,<sup>46</sup> and the conclusion has been reached that both the heterogeneous and the homogeneous reaction can be studied if the conditions are carefully controlled, without interference by the exchange reaction.

Kistiakowsky<sup>26</sup> has continued his studies of thermal *cis-trans* isomerizations. Since free radicals are known to react easily with double bonds, it seems extremely desirable to investigate whether or not radicals play a role in such changes.

Littmann<sup>35</sup> has studied the thermal decomposition of some unsaturated bicyclic compounds, and has shown that the C-C bond next to the double bond is stronger than normal, whereas the next C-C bond is weaker than normal.

The thermal decomposition of nitrogen chloride has been studied<sup>80</sup> between  $150^\circ$  and  $250^\circ \text{C}$ .; it is homogeneous, follows a bimolecular law, and has an activation energy of 24 calories.

\* Rice, F. O., and Dooley, M. D., *J. Am. Chem. Soc.*, **56**: 2747 (1934).

† Geib, K. H., and Harteck, P., *Z. phys. Chem.*, **170A**: 1 (1934).

O. K. Rice and Sickman<sup>55</sup> report the induced decompositions of propionic aldehyde and isobutane by azomethane. Several percent of azomethane cause decomposition of only part of the propionic aldehyde, so that this cannot be a "degenerate explosion" as suggested by Semenov.\* The same authors find that, at 300° C., ethylene is rapidly polymerized by small quantities of azomethane, the rate being proportional to the square root of the azomethane pressure and to the three-halves power of the ethylene pressure.<sup>55</sup>

The photolysis of azomethane was studied;<sup>14</sup> the quantum yield was found to approach unity as its upper limit and to be independent of temperature up to 226° C., so that no reaction chain occurs in this temperature interval. The photochemical decomposition products formed at 30° C. and the thermal decomposition products at 300° C. seem to be the same.<sup>18</sup> Mercury vapor has no effect on the rate.

Glyoxal<sup>66</sup> decomposes at a measurable rate in the range 410 to 450° C.; the reaction is homogeneous and first order; however, the reaction cannot follow any simple scheme, such as  $C_2H_2O_2 \rightarrow CO + HCHO \rightarrow 2CO + H_2$ , because carbon and tar are formed during the course of the decomposition, as well as a large amount of condensible products.

At least half of the process of the thermal decomposition of alkyl halides can be attributed to a unimolecular dissociation; in the case of methyl iodide, the recombination reaction is more important than inter-radical reactions.<sup>68</sup>

The decomposition of ethyl nitrite<sup>50</sup> seems to be a curious example of a primary dissociation into a molecule and a radical, followed by reaction of this with the substrate. No chain reaction should occur, because of decomposition of the radical  $CH_3CHONO$  into the two molecules, namely, acetaldehyde and nitric oxide. Steacie and Shaw have shown<sup>69</sup> that propyl nitrite decomposes in a similar manner to its two lower homologs.

Sickman and O. K. Rice have studied<sup>62</sup> the thermal decomposition of propylamine in the pressure range between a few tenths of a mm. to over 100 mm. The reaction is probably a chain, but it was not found possible to give a satisfactory explanation of its course.

West<sup>81</sup> has decomposed methyl iodide, acetone, propionic aldehyde and benzene photochemically in the presence of a 1:1 ortho-para hydrogen mixture. The results indicated the production of radicals by methyl iodide and acetone, but not by propionic aldehyde and benzene. This is strong evidence in support of Norrish's views\* on the photochemical dissociations of aldehydes and ketones.

H. A. Taylor and coworkers<sup>76, 77</sup> find that the decompositions of diethyl- and triethylamines probably involve the formation and

\* Semenov, N. N., *Z. phys. Chem.*, **28B**: 62 (1935).

\* Norrish, R. G. W., *Trans. Faraday Soc.*, **30**: 107 (1934).

subsequent decomposition of substituted hydrazines but the exact mechanism is not clear.

The decomposition of nitromethane<sup>78</sup> proved to be an extremely complex reaction, in which nitrosomethane and its isomer, formaldoxime, are intermediate products.

Mead and Burk<sup>87</sup> studied the thermal decomposition of benzene in a flowing system and report that it is a heterogeneous bimolecular reaction, whereas Pease and Morton<sup>†</sup> had previously reported the decomposition as homogeneous and first order.

F. O. Rice and Polly<sup>49</sup> made a preliminary study of the decomposition of mercury diheptyl and conclude that the heptyl radical decomposes, at least to some extent, into cyclohexane plus methyl radicals.

Egloff and Wilson<sup>10</sup> have reviewed the thermal reactions of paraffins, olefins, acetylenes, and cycloparaffins.

Lang and Morgan<sup>29</sup> have studied the pyrolysis of propane in the presence of water vapor and conclude that their experimental results are best explained on the basis of Nef's hypothesis. A similar study on pentane<sup>38</sup> showed that the results could be explained by a primary decomposition into radicals, followed by a chain.

**Halogenations.** The photochlorination of gaseous ethylene has been studied<sup>72</sup> and found to have many of the characteristics of a chain reaction; probably chlorine or the complex  $\text{Cl}_3$  or both are intermediaries. One curious result observed was that the chlorination of ethylene in an ethylene-hydrogen mixture proceeds without formation of appreciable quantities of hydrogen chloride. Willard and Daniels<sup>82</sup> have studied the effect of oxygen in the photobromination of tetrachloroethylene and have proposed a mechanism for the reaction.

The thermal reaction between formaldehyde and chlorine has been discussed<sup>27, 28, 65</sup> and certain similarities with the photochemical reaction pointed out, such as the possible formation of formyl chloride as an intermediate.

Yuster and Reyerson<sup>83</sup> have studied the homogeneous chlorination of propane and found that the reaction exhibits all the peculiarities of the chain type. The photochlorination of liquid pentane is a chain.<sup>71</sup>

**Oxidations.** The hydrogen-oxygen reaction\* has been made the subject of several detailed and critical discussions especially by Kassel and Storch,<sup>24</sup> who studied the thermal reaction of oxygen with both hydrogen and deuterium. Smith and Kistiakowsky<sup>63</sup> have studied the photochemical hydrogen-oxygen reaction and Lind and Schiflett<sup>34</sup> have studied the rate of combination of oxygen and deuterium under the influence of alpha-rays. Cook and Bates<sup>7</sup>

<sup>†</sup> Pease, R. N., and Morton, J. M., *J. Am. Chem. Soc.*, **55**: 3190 (1933).

\* See Kassel, "Annual Survey of American Chemistry," VIII: 27 (1933).

have examined the reaction of hydrogen and deuterium atoms with molecular oxygen, by studying the photo-oxidation of hydrogen and deuterium iodides.

Rodebush and Spealman<sup>57</sup> suggest that recombination of hydrogen atoms in presence of hydrogen chloride is due to the reaction  $H + HCl \rightarrow H_2 + Cl$ , followed by a rapid reaction between chlorine and hydrogen atoms to reform hydrogen chloride.

The rate of oxidation of carbon monoxide catalysed by nitrogen dioxide appears to be determined at low concentrations of the catalyst by a chain mechanism and at higher concentrations by the trimolecular oxidation of nitric oxide.<sup>8</sup>

The oxidation of gaseous glyoxal has been studied<sup>67</sup> and appears to proceed through the intermediate formation of an activated peracid.

The oxidation of 2-butene gives<sup>36</sup> mainly acetaldehyde and butadiene and not methyl ethyl ketone, as might be expected on the basis of the hydroxylation theory.\* A mechanism of the reaction is proposed. Small amounts of oxygen have been found to accelerate greatly the reaction of ethylene-hydrogen mixtures; the effect is probably to accelerate the hydrogenation, rather than the polymerization, of the ethylene.<sup>47</sup>

Pease<sup>45</sup> has studied the slow oxidation of propane in a reaction tube coated with potassium chloride. This largely eliminated peroxide formation, the primary products being methanol, formaldehyde, carbon monoxide, and water. The results could be formulated by using a radical chain mechanism† in which the methoxyl and propyl radicals are the chain carriers. When the oxidation of propane is conducted in bulbs not coated with potassium chloride, there is a long induction period.<sup>41</sup>

Chapman<sup>5</sup> has studied the oxidation of chloroform, using chlorine as a photosensitizer; the products are phosgene and hydrogen chloride; the reaction is clearly a chain but enough data have not yet been accumulated to determine completely the mechanism. Both the thermal and photochemical oxidations produce an intermediate peroxide, which yields initially chlorine and finally hydrogen chloride and phosgene.<sup>6</sup>

**Polymerizations.** H. A. Taylor and Van Hook<sup>75</sup> have studied the polymerization and hydrogenation of acetylene and conclude that in each reaction the principal process is bimolecular. On the other hand, Jungers and H. S. Taylor<sup>21</sup> conclude that the mercury photosensitized polymerization of acetylene is a process involving short chains. The rates of polymerization of acetylene and deuterio-acetylene are equal within the limits of experimental error.<sup>33</sup>

O. K. Rice and Sickman<sup>55</sup> have found that ethylene is rapidly

\* Bone, W. A., and Wheeler, R. V., *J. Chem. Soc.*, **85**: 1637 (1904).

† Rice, F. O., and Rice, K., "The Aliphatic Free Radicals," Baltimore, The Johns-Hopkins Press, 1935, 204 p.

polymerized by small quantities of azomethane at about 300° C. Storch <sup>74</sup> concludes that the ethylene polymerization is not a simple bimolecular reaction; traces of impurities exert such a marked effect that it was not found possible to obtain reproducible results even with "pure" ethylene.

**Atomic Reactions.** The question as to the nature of the primary process in chemical reactions is still very much to the fore, and was discussed in considerable detail at a symposium on reaction kinetics held during the New York meeting of the American Chemical Society. Kistiakowsky <sup>25</sup> reviewed the present theory of truly unimolecular reactions, presented the experimental facts, and finally gave a list of decompositions and isomerizations which go homogeneously in the gas phase without chains. F. O. Rice <sup>48</sup> reviewed the subject of organic decompositions from the standpoint of free radical formations and the initiation of chains.

Jackson <sup>20</sup> has proposed various mechanisms to account for the formation of carbon dioxide and hydrogen peroxide when carbon monoxide reacts with the products of a water vapor discharge tube.

Lewis and von Elbe <sup>32</sup> have collected data that include the reaction energies of a number of the simpler elementary reactions. Morris and Pease <sup>40</sup> agree with the accepted Christiansen-Herzfeld-Polanyi mechanism for the HBr formation and take as heats of activation  $\text{Br} + \text{H}_2$ , 17.7 Kcal;  $\text{H} + \text{HBr}$ , 1 Kcal; and  $\text{H} + \text{Br}_2$ , 1 Kcal. For the photochemical formation of HCl, they take, with Bodenstein,  $\text{Cl}_2 + h\nu = 2 \text{Cl}$ ,  $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$  (6 Kcal);  $\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl}$  (2-3 Kcal);  $\text{H} + \text{HCl} = \text{H}_2 + \text{Cl}$  (5 Kcal);  $\text{H} + \text{O}_2 = \text{HO}_2$  in three-body collisions or  $\text{H} + \text{HCl}$  on a surface is assumed as the chain-breaking mechanism. Finally,  $\text{H} + \text{HI} = \text{H}_2 + \text{I}$  (1 Kcal);  $\text{H} + \text{I}_2 = \text{HI} + \text{I}$  (0 Kcal),  $\text{I} + \text{H}_2 = \text{HI} + \text{H}$  (33 Kcal).

Spealman and Rodebush <sup>64</sup> have studied the reactions of nitrous and nitric oxides with both atomic oxygen and atomic nitrogen.

Oldenberg <sup>43</sup> has made a study of the free hydroxyl radical and agrees with Urey and Lavin \* that it can be pumped out over considerable distances from a water-vapor discharge tube.

**Bond Energies.** Deitz <sup>9</sup> has discussed the bond energies of hydrocarbons and Serber <sup>60</sup> has calculated the energies of a number of hydrocarbon molecules and compared the calculated and observed values.

Rossini <sup>58</sup> has estimated the heat of formation of neopentane from the heats of formation of the two isomers of butane.

Laséreff <sup>30</sup> has suggested the very high value of 123 calories for the carbon-carbon bond but this conclusion has been questioned by Gershinowitz, <sup>15</sup> who prefers the older figure of 77 calories.

Nilsen <sup>42</sup> calculates the electron affinity of certain radicals containing aromatic rings. Starting out with the benzyl ion, he cal-

\* Urey, H. C., and Lavin, G. I., *J. Am. Chem. Soc.*, 51: 3290 (1929).

culates the "exchange" energy between the eight non-bonding electrons (6 from the ring, one from the  $\text{CH}_2$  group, one as negative charge) and subtracts the energy for seven electrons (the uncharged radical). Electron affinities of more complicated cases (e.g., triphenylmethyl) are then found by the use of a formula of Pauling and Wheland, permitting their calculation from the values of the constituents. The comparison with experiment shows the theoretical values to be too high.

Nilsen then draws more qualitative conclusions about the ability to form ions and emphasizes the much stronger tendency of radicals containing a double bond besides a benzene ring to form ions, as compared with the same tendency without the double bond; for example, the cinnamyl radical has seven possible structures giving resonance, while the hydrocinnamyl radical has only two (two arrangements of double bonds in the ring). Hylleraas<sup>19</sup> strongly attacks Nilsen's method of calculation.

Pauling and Wheland<sup>44</sup> agree with this criticism and emphasize that the main contribution to the electron affinity should come from the changed coulomb attraction, the difference in exchange energy being very small.

Sherman, Sun, and Eyring<sup>61</sup> discuss the addition of hydrogen to benzene. The first method, which assumes that, in the activated state, the electrons involved in the double bonds and those in the  $\text{H}_2$  resonate between fourteen different combinations, gives a heat of reaction of +85 Kcal. (absorbed by the addition), while the experimental value is slightly negative. The heat of activation is found to be 96 Kcal. Better agreement results if one assumes with Pauling and his coworkers a directed valance, namely interaction of only the four neighboring electrons, two from  $\text{H}_2$  and two from the disappearing double bond. If one takes the energy of the CH bond as 120 Kcal., the heat of reaction is found to be -11 Kcal, that of activation 78. Similarly, these heats are calculated for the adsorption of  $\text{C}_6\text{H}_6$  (-5 and 3 Kcal.) and  $\text{H}_2$  (-4.6 and 24 Kcal.). The authors point out that the usual bond energy of CH is much smaller than 120 Kcal., the value for the free C-H radical, due to the repulsion of the other atoms in the molecule which weakens the bond.

**Explosions.** The explosion of azomethane<sup>1</sup> seems to follow the simple Semenov theory,\* in which the rate of generation of heat by the reaction is faster than the rate of removal of heat. The explosion of ethyl azide<sup>4</sup> also appears to be a pure thermal one; however, the decomposition of ethyl azide may occur through a chain with the imposed condition that the chains cannot branch. The induction times in the cases of such explosions as azomethane and ethyl azide have been studied<sup>52</sup> and it has been found possible to calculate rough values for the heats of decomposition of the substances.

\* Semenov, N., *Z. Physik*, 48: 571 (1928); *Z. physik. Chem.*, 2B: 161 (1929).



Storch<sup>78</sup> has shown that the low pressure explosion limit of methane-oxygen mixtures is very sensitive to the nature of the surface of the containing vessel.

Scorah<sup>59</sup> discusses the thermodynamic theory of detonation and Lewis and von Elbe<sup>31</sup> calculate explosion pressures in hydrogen-oxygen mixtures. Explosions in presence of the inert gas, helium, permits the heat of dissociation of water into H and OH to be calculated.

**Theoretical.** About twenty years ago, Trautz took the "constant" factor  $A$  in front of the exponential in the expression of the

reaction velocity,  $k = A \exp \left( -\frac{E}{RT} \right)$ , to be the number of collisions

for bimolecular reactions and pointed out that  $A$  for unimolecular reactions is always of the same order of magnitude. Approximate theories were given for this fact, but further experiments showed a variation between  $10^{10}$  and  $10^{15}$ . An approach to this problem was made by Rodebush\* and O. K. Rice and Gershinowitz.<sup>†</sup> The latter have pursued the subject in papers discussed later on. Eyring and his coworkers have taken the matter up from a systematic viewpoint that permits clear understanding. Whenever<sup>12</sup> there exists a heat of activation, there must exist a system, the "activated complex," having at least this energy, which is sufficient for reaction. If one considers the energy surface which gives the total mutual potential energy of all the reaction participants as function of the coordinates, there must be a flat saddle dividing the regions before and after the reaction. If one is able to calculate the concentration,  $n'$ , of the activated complex, then the numbers passing the saddle, i.e., reacting, are given by this concentration,  $n'$ , times the velocity across the saddle, namely,  $\left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}}$ . The

variation of  $A$  is therefore mainly a variation of  $n'$ ;  $n'$  is calculated statistically. The statistical weight of a state is proportional to the phase volume allotted to it, which, for high temperatures, is for translation under standard conditions  $\propto 3.5 \times 10^{-7}$  (distance between molecules) for rotation  $\propto 10^{-7}$  (circumference of a molecule), for a molecular vibration  $\propto 10^{-9}$  cm (amplitude). Therefore  $n'$  (and  $A$ ) will be greater, the more translations or rotations compared with vibrations the activated state has. The ratio of the phase integral of the activated complex to that of the initial substances gives the relative concentration of the former. In the case of unimolecular decompositions, one leaves out in the phase integral of the activated complex the bond that breaks, considering it as having been already changed into translation. The contribution it gives, together with the velocity factor, results in a factor  $kT/h$ .

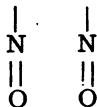
After the discussion of some general cases, namely,  $A + BC \rightarrow A - B$

\* Rodebush, W. H., *J. Chem. Phys.*, 1: 440 (1933).

† Rice, O. K., and Gershinowitz, H., *J. Chem. Phys.*, 2: 853 (1934); Gershinowitz, H., and Rice, O. K., *ibid.*, 2: 273 (1934).

$-C \rightarrow AB+C$ ,  $A+BC+D \rightarrow A B C D \rightarrow AB+CD$  in the first paper, the next task is the actual calculation of the activated complex in specific cases. This can be done either by calculating the energy surface theoretically or by taking the properties of the activated complex from similar molecules.

As examples of the case where the properties of the activated complex are reconstructed from those of similar molecules, the reactions  $2NO+O_2 \rightarrow 2NO_2$  and  $2NO+Cl_2 \rightarrow 2NOCl$  are considered.<sup>16</sup> In the former, the activated complex  $N_2O_4$  is taken to have the form



and to have, besides three translations and a fourth along the breaking bond, three external and one internal rotations and ten vibrations, compared with nine translations, six rotations and three vibrations of the 3 molecules NO, NO,  $O_2$ . Of these frequencies, seven are taken from the known frequencies of  $N_2O_4$  and three are considered too high to be of importance in the range of temperatures used. The result for  $A$  is a decrease with temperature, due to the strong temperature increase of the phase integral of the 15 translations plus rotations of the original molecules, while the corresponding vibrations of the activated complex are largely suppressed by the quantum theory. It turns out that if  $\epsilon$ , the activation energy at  $T=0$ , is put zero, the value of  $A$  so calculated represents the measurements well, both in their absolute value and the dependence on  $T$ . In the second reaction, the activated complex is taken to be of similar form as in the preceding case, but as no stable molecule,  $(NOCl)_2$ , is known, the frequencies have to be estimated. In this case the assumption of an activation energy of 4780 cal. represents the facts well.

The next problem<sup>70</sup> is the decomposition of nitrous oxide into  $N_2+O$ . Here the energy surface can be calculated theoretically, as the potential energy curve of nitric oxide as function of the N—O distance is known. However, the O atom would leave the  $N_2O$  molecule in the  $d$ -state (i.e., with a resultant orbital quantum number 2) if it dissociated without change of the electron structure. Furthermore, this state is so highly excited, that much more energy would be necessary. The O-ground state has one orbital quantum ( $p$ -state), but can not be bound to  $N_2$ . The potential curves for the attraction  $N_2-O$  ( $d$ ) and repulsion  $N_2-O$  ( $p$ ) intersect, and at this place a transition between the two states is possible. The height of this intersection gives an activation energy of 52 kcal, compared with the experimental value of 53. The small probability of the transition between the two curves, which belong to two different systems of levels (triplet and singlet), introduces a new factor, small compared with one, into the reaction velocity. It can be determined only by division of the experimental reaction velocity through the theoretical one and turns

out to be  $2 \times 10^{-4}$ . Theoretically, it depends on an interaction energy, probably between the spins. This must be about 5 cal./mole, a reasonable amount, to give the above transition probability. Other cases of change of electron level multiplicity are discussed.

A new problem<sup>13</sup> turns up in the recombination of atoms without hump in the curve of mutual potential energy. Such an activation energy, i.e., such a hump, arises however, from a consideration of the *rotation* of the activated complex. For a given quantum number of rotation  $n$ , the energy of rotation is  $\frac{h^2}{8\pi^2} I^{-1}n^2$ , where  $I$ , the moment

of inertia, is proportional to the square of the dimensions. On approach, the rise of the attractive (negative) potential energy plus the rise of the positive energy of rotation gives a maximum at a distance, which depends on  $n$ . Upon averaging over the different states, the authors find that hump at 500° K. if the atoms are 4.5 Å apart.

They first investigate the reaction  $H_2 + H \rightarrow 3H$ . The simplest case is one where all three atoms lie in a straight line. The potential surface for this case had been calculated before.

The activated complex has two degrees of freedom of rotation and two of transversal vibrations. The motion in the line of the three atoms is such that the main contribution comes from cases where the two hydrogen atoms of the molecule are not in their normal position, but farther apart, so that their mutual potential energy is  $\propto 45$  kcal. They are to be hit by an atom of kinetic energy, such that the total energy is higher than the dissociation energy plus the small activation energy coming from the rotation. As soon as the incoming atom has approached to a distance equal to that of the two other atoms, its kinetic energy is redistributed, part of it going over into the vibration. If enough goes over, dissociation occurs, but in about  $\frac{7}{8}$  of the collisions with sufficient energy the redistribution is not sufficient for the reaction to occur. Next the case of the third atom arriving normal to the axis of  $H_2$  is investigated and found to give a smaller contribution than the one first discussed. The theoretical result for the inverse reaction (recombination of 2 H with H as third body) is found so to be  $\propto 3 \times 10^{15}$ , while the experiment gives  $1.2 \times 10^{16}$ . Helium as third body is then discussed and it is pointed out that the efficiency as third body is connected with reactivity.

In a lecture<sup>11</sup> at the Symposium at the American Chemical Society meeting in New York, Eyring gives a review of the historical development and of his own theory and then applies it to reactions in condensed systems. As the velocity is determined, apart from the factor  $\frac{kT}{hm}$ ,

by the equilibrium concentration of the activated complex, one can put the concentration-ratio of the activated complex and the original substances in solution equal to that in the gas times the ratio of the solubility of the activated complex to that of the original substances. If,

in a monomolecular decomposition, the original molecule and the activated complex are very similar, their solubility will be equal and the reaction velocity equal in gas and solution. In other cases, the solubility of the activated complex is estimated from that of a similar, stable molecule or calculated backward from measured velocities.

Kassell<sup>22</sup> raises the objection that during the short life of the activated complex no full quantization might take place. While this objection seems justified, it seems that the important shortlived bonds have usually so low frequencies that classical formulas are sufficient and then the degree of quantization does not matter. Rodebush<sup>56</sup> draws attention to the historical development.

O. K. Rice and Gershinowitz,<sup>53</sup> who have the great merit of having started the detailed application of statistics to this problem, continue the development of their method, which does not include the consideration of the activated complex at first. They first calculate the probability of a given quantum state. Then they classify the degrees of freedom into those which are not affected by the reaction and those that are. Of the first, all quantum states are assumed to be able to react. Therefore one has to sum up over these, whereby the phase integral over these quantum states drops out of the reaction constant. The assumption which the authors think most probable is that, for a dissociation, one quantum state of the vibration along the bond that is to be broken is available and all states in the other degrees of freedom. Conversely for the association, all the quantum states in the fragments are available except of those rotations that will not be possible after reunion. Of these degrees of freedom, only those quantum states can react, which, taken together, have an entropy equal to that of the vibration to be formed. A reaction following these prescriptions is said to occur with complete orientation. This theory is applied to the following cases. Decomposition of alkyl iodides: theory  $A = 1.5 \times 10^{13}$ ; experimental values for various alkyls,  $3.9 \times 10^{12}$ ;  $1.8 \times 10^{13}$ ,  $2.8 \times 10^{13}$ . Decomposition of alkyl nitrites: theory  $2.4 \times 10^{13}$ ; experimental values,  $0.9 \times 10^{13}$ ;  $7.0 \times 10^{13}$ . Tertiary butyl alcohols:  $1.2 \times 10^{14}$ ; experimental value,  $4.8 \times 10^{14}$ . In addition, tertiary amyl alcohol is treated. Then the mechanisms for the isomerization of cyclopropane and the decomposition of  $\text{ClCOOCCl}_3$  are discussed and found to be in good agreement with the hypothesis. In contrast, the decomposition of certain esters shows much lower values, which is explained by the formation of an activated complex with less internal free rotations than the original molecule. In the decomposition of azoisopropane, the hypothesis gives again the right magnitude, but for azomethane, the rate is  $10^3$  times too high, which is explained by saying that no orientation is necessary for the methyl group. The authors point out that their formulas for exact orientation are identical with Eyring's, provided that the activated complex is in every respect, except the vibration along the breaking bond, identical with the decomposing molecule. They have been very successful in selecting the right assumptions,

but a further theoretical discussion seems desirable to the reviewer.

As Rice and Gershinowitz define the heat of activation not as that at  $T=0$  but as the average value at  $T$ , it varies with temperature, a variation connected with that of the factor  $A$  in front of the exponential. They show now<sup>54</sup> that the new formula discussed above leads to the same consequences as Kassel's theory for the dependence of the rate of unimolecular reaction on the energy the molecule has above the minimum activation.

O. K. Rice<sup>51</sup> investigates the problem of inelastic collisions between two atoms, i.e., such collisions that the electron structure is changed. He considers the two atoms as an unstable molecule, and the two states of the atomic electron system as two different electron states of the molecule, both of which are repulsive. The transition probability between these two repulsive states at the place where the two energy-atomic distance curves intersect gives then the probability of excitation. The discussion of the general mathematical features show that the problem is not yet solved.

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## Chapter III.

### Molecular Structure.

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This section covers most of the material formerly grouped under the title "Subatomics." With the tremendous growth of nuclear physics, to which the name subatomics properly belongs, it was felt necessary to change the title of this section. Crystal structure, although it is of course of great importance in the study of molecular structure, is too large a field to be included.

**Electron Diffraction by Gas Molecules.** The structures of chlorine monoxide, oxygen fluoride, dimethyl ether, 1,4-dioxane, methyl chloride, methylene chloride, and chloroform,<sup>8</sup> germanium tetrachloride,<sup>1</sup> 4,4'-diiododiphenyl ether, phosphorous ( $P_4$ ), and arsenic ( $As_4$ ),<sup>5</sup> sulfur dioxide, carbon disulfide, and carbonyl sulfide,<sup>4</sup> nickel carbonyl,<sup>3</sup> phosgene, vinyl chloride, 1,1-dichloroethylene, *cis*-dichloroethylene, *trans*-dichloroethylene, trichloroethylene, tetrachloroethylene, thiophosgene,  $\alpha$ -methylhydroxylamine, and nitromethane<sup>2</sup> have been obtained by electron diffraction studies during the past year.

Several methods of interpreting the experimental photographs are used by the two groups of American workers. One method is to compare the calculated intensity of scattering based on an assumed model with the experimental values obtained from densitometer curves by the use of plate calibrations.<sup>5</sup> The difficulties of this method are the extent of the calculations necessary, the calibration requirement, and the fact that no true maxima occur on the curves, so that they are difficult to compare. The latter defect may be remedied by multiplying each curve by a certain factor which changes the slight prominences of the curves into true maxima. The simplest method of interpretation\* is based on the assumption that the visual maxima (psychological) observed on the photographs can be identified with the maxima of a very much simplified form of the theoretical function. There is a certain amount of evidence that this much easier method yields reasonably accurate results. Recently a quite different approach has been developed,<sup>6</sup> in which no preliminary model needs to be postulated. Instead, visual ring diameters and esti-

\* Pauling, L., and Brockway, L. O., *J. Chem. Phys.*, 2: 867 (1934).

mated ring intensities are taken from the photograph and used to calculate a *radial distribution curve*, based on a simplified approximation to a treatment developed earlier for crystal and liquid studies. The maxima in this curve give the prominent internuclear distances in the molecule to a claimed accuracy of a few percent.

There is not sufficient space to discuss the many interesting conclusions which have been drawn from these structure determinations. One such discussion,<sup>7</sup> however, has been published which treats chiefly the effect of resonance on bond distances, resonance between a single and a double bond yielding a distance intermediate between the single and double bond distances but more nearly the double bond value.

**The Raman Effect.** There has been strong emphasis on deuterium derivatives in the experiments on the Raman effect carried out during the year, Raman spectra of  $H_2$ , HD and  $D_2$ ,<sup>20</sup>  $C_2D_2$ ,<sup>12</sup>  $CH_3D$ ,<sup>16</sup>  $CDCl_3$ ,<sup>22</sup>  $C_6D_6$ ,<sup>21</sup> and  $(CH_3)_3CCH_2D$ <sup>18</sup> having been obtained. Of these only the three forms of the hydrogen molecule were examined in the gas phase with sufficient resolving power to show the rotational lines. The vibrational lines of all these molecules, when used with the known vibration lines of the ordinary light molecules, have given valuable assistance in the problem of assigning each observed line to a definite mode of vibration of the molecule, or to combinations or overtones thereof. In addition, more information concerning the form of the molecular potential energy function can be obtained if the data for the isotopic molecules are available. Both of these types of information are important in thermal calculations, the former because the degeneracy of each level is needed, the latter because inactive frequencies must often be calculated.

$H_2O$  in the gas phase was studied again,<sup>10</sup> with the detection of but one line. There still remains a discrepancy between the Raman frequency observed and that calculated from the infrared data. Two trichloroethanes have been studied in the liquid phase,<sup>14</sup> as well as eight compounds related to tetramethylmethane.<sup>18</sup> Oxalic acid has been measured<sup>13</sup> both in the crystalline form and in solution in water and alcohol. 1,3-Cyclohexadiene has been observed.<sup>17</sup>

The Raman effects of sulfuric acid,<sup>9</sup> orthophosphoric acid,<sup>15</sup> and magnesium sulfate,<sup>11</sup> all in water solutions, have been published. In the last of these no shift of the strong line with concentration was found, while with the others a slight and gradual shift was observed. Zinc chloride and bromide were observed as fused salts.<sup>19</sup>

**Infrared Absorption Spectra.** The experimental results in infrared spectroscopy will be taken up in the order of the complexity of the molecules involved. The rotational fine structure of the low frequency fundamental of DCN when compared with the similar band of HCN leads to interatomic distances of 1.06 Å and



1.15 Å for the H-C and C-N distances, respectively.<sup>33</sup> The data available also sufficed for a calculation of the four vibrational force constants, enabling the missing fundamental of DCN to be estimated as 1896.7  $\text{cm}^{-1}$ . New vibration-rotation bands for carbonyl sulfide have made possible an evaluation of the ten constants in the expression for the vibrational energy as a function of the quantum numbers (including quadratic or anharmonic terms in  $V_1$ ,  $V_2$ , and  $V_3$ ).<sup>33</sup>

The problem of the water molecule is not yet completely solved, although a great deal is known of its spectrum and structure. A re-examination of the pure rotation spectrum of  $\text{H}_2\text{O}^{30}$  gave results in quite good agreement with Mecke's term values obtained from the photographic infrared, although the latter are not sufficient to account for all the lines.  $\text{D}_2\text{O}$  has been studied,<sup>27</sup> also HDO, so that now eight of the nine fundamental frequencies for the three species of water are known. The fine structure of certain of the  $\text{D}_2\text{O}$  and HDO bands was also obtained. The theory of the asymmetric top needs to be further refined if it is to fit all the data accurately, but it seems clear that the water molecule is an isosceles triangle with angle of roughly  $105^\circ$  and O-H distance of about 0.95 Å. A very thorough study<sup>37</sup> of the fine structure of the infrared band at 10,100 Å of the similar molecule  $\text{H}_2\text{S}$  yields an angle of about  $92^\circ$  and a H-S distance of 1.345 Å. The method used was to compute the theoretical line frequencies from an assumed model, derive equations for the effect of small changes in the molecular constants, and then to solve these equations by least squares, using the observed data. A rough correction for centrifugal expansion was included.

The vibrational assignments for acetylene, for which a great deal of data exists, are not absolutely unambiguous as yet, although a new band at 7989 Å has been reported.<sup>35</sup>

The structure of ammonia is believed to be a flat, symmetrical pyramid with altitude of about 0.4 Å and base of about 1.59 Å on a side. These figures have been obtained from a study of  $\text{NH}_3$  and  $\text{ND}_3$  in the infrared. The pure rotation spectra of these two species has been mapped from 40  $\mu$  to 170  $\mu$ .<sup>28</sup> The low frequency fundamental for each of the four possible species is double,<sup>25</sup> as required by theory for a molecule capable of inversion (turning inside out). Most of the observed bands of ammonia, especially in the photographic region,<sup>24, 36</sup> have not been analyzed and classified with certainty, probably in part because they are complicated by the interaction of rotation and vibration<sup>71</sup> and by inversion.<sup>74</sup>

An important series of papers<sup>40, 44, 45</sup> on the methane-type molecules, methane, silane, and germane, shows that the fine structure of the fundamental bands is much more complicated than previous measurements (on methane) with lower dispersion had indicated.

Whether this is due to absorption by excited molecules, or to the breaking down of the degeneracy of the energy levels by the distortion of the tetrahedron during vibration, is as yet unknown. The six fundamental frequencies of  $\text{CH}_3\text{D}$  have been found and resolved.<sup>38</sup> One of the parallel vibrations yields a particularly clear band from which one of the moments of inertia and hence the molecular dimensions can be obtained. The C-H distance is 1.093 Å. This molecule, being the simplest symmetric top not complicated by inversion, deserves extensive study.

The low frequency fundamental bands (essentially a  $\text{CH}_3$  against X vibration) for  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  have been found and resolved into P, Q, and R branches but only for  $\text{CH}_3\text{Cl}$  partially into lines.<sup>26</sup>

With the preparation and study of  $\text{C}_6\text{D}_6$ , the benzene problem has been greatly clarified. The infrared spectrum has been obtained,<sup>31</sup> and the Raman results are mentioned elsewhere. Whereas, formerly, certain European investigators believed the spectroscopic results incompatible with the conventional plane hexagon structure, there now remains little doubt of its correctness. The assignment of all the active fundamental frequencies to the theoretical modes of vibration is fairly certain and a set of approximate force constants for the bonds is available.\* Further evidence for the plane structure is provided by a search<sup>29</sup> of the far infrared which yielded no fundamental bands, such as would be expected to appear for the models of lower symmetry.

Work in solutions<sup>39</sup> and pure liquids<sup>34</sup> indicates empirically that the CN group in cyanides and nitriles has a characteristic absorption region at about  $4.4\ \mu$  with perhaps another at  $7\ \mu$ . A large number of natural substances, as well as the liquids carbon tetrachloride, ethylene chloride, ethylbenzene, *o*-dichlorobenzene, ethyl acetate, propyl bromide, butyl bromide and pentachloroethane, have been measured in the infrared from 1 to  $15\ \mu$ .<sup>43</sup> An extensive study<sup>46</sup> of the absorption of a large number of organic compounds in carbon tetrachloride solution in the region  $6000$  to  $7400\ \text{cm}^{-1}$  has yielded considerable information regarding the characteristic absorption bands associated with the OH, NH, and CH groups. The results have been applied to the problem of chelation,<sup>39a</sup> since it is found that these characteristic absorptions are greatly reduced by chelation.

A paper<sup>32</sup> dealing with both the experimental results for the absorption of crystalline MgO and the theory of the absorption of crystals in general shows that there are many secondary absorption maxima for cubic crystals instead of just one as previously believed. This is explained on the basis of anharmonic forces between the atoms, which break down the simple selection rules. The absorption of solid HCl<sup>42</sup> in the  $3.7\ \mu$  region shows a fine

\* Kohlrausch, K. W. F., *Z. physik. Chem.*, 30B: 305 (1935).

structure, probably not completely resolved, differing from that of gaseous HCl.

The optical dispersion of gaseous HCl between 1 and  $10\mu$  has been measured<sup>41</sup> with results indicating that the effective charge for the vibrator-rotator is  $(1.00 \pm 0.05) \times 10^{-10}$  e. s. u., which is too small to explain the discrepancy between the polarization obtained from the index of refraction extrapolated to infinite wavelength and that from the temperature invariant part of the dielectric constant.

**Ultraviolet Absorption Spectra.** A good many papers giving experimental data have appeared during the year. One series gives the results for the far ultraviolet for  $O_2$ ,<sup>60</sup>  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,<sup>58</sup>  $CH_3Br$ ,  $CH_3Cl$ ,<sup>59</sup>  $CH_3I$ ,<sup>57</sup>  $C_6H_6$ ,  $C_6D_6$ ,<sup>61</sup>  $C_2H_5Cl$ ,  $C_2H_5Br$ ,  $C_2H_5I$ ,<sup>56</sup>  $H_2O$ , and  $H_2S$ .<sup>55</sup> In some of these it was possible to fit the results into a Rydberg series and thus find the ionization potential. Acetone,<sup>49</sup> *cis*- and *trans*-dichloroethylene,<sup>53</sup>  $NH_3$ ,<sup>51</sup> and  $ND_3$ <sup>52</sup> have likewise been studied in the ultraviolet. A summary<sup>50</sup> of vibration frequencies in excited states indicates that the strong frequencies all correspond to symmetrical vibrations. The  $SO_2$  spectrum has been examined and an assignment of vibrational quantum numbers given.<sup>47, 48</sup>

In this brief survey it has been necessary to omit many papers dealing with diatomic spectra, of most interest to physicists (except for thermodynamic results), and other papers in which the ultraviolet spectra of very complicated molecules were used as an empirical tool.

**Theory of Molecular Vibrations and Rotations.** The past year has been characterized by an increasing realization that the intuitive application of the equations for the rotational energy levels of a rigid top to the data for real molecules has not been based on any sound theoretical treatment. In a sequence of papers<sup>80, 67</sup> such a treatment was given, to a certain order of approximation, resulting in the conclusion that the ordinary formulas are approximately applicable if, and only if, the coupling of the angular momenta of rotation and vibration is taken into account. This latter effect has been known for some years but has not been sufficiently emphasized until quite lately. A detailed study of the coupling of the angular momenta in methane and ammonia has been made,<sup>66, 71</sup> with a comparison of theory and experiment which is generally favorable but which shows some discrepancies.

There is still lacking a complete mathematical treatment of polyatomic molecules comparable to that which exists for diatomic molecules, even assuming harmonic binding, but it is now recognized that the problem is not as simple as formerly believed. A group theory discussion<sup>83</sup> has been given which indicates that the splitting of fine-structure lines observed for certain symmetrical molecules<sup>40, 45</sup> may possibly be due to some of the neglected terms

in the mathematical treatment. This discussion was based on an earlier group theory treatment<sup>82</sup> of the permutation symmetry of polyatomic molecules which yielded a complete and general method of calculating the statistical weights of the rotational states, formerly obtained for molecules such as methane only by very difficult arguments.

A number of papers on molecular vibrations have appeared. Mechanical models<sup>75, 79</sup> have been built and observed in an effort to interpret the spectra of benzene and some of its derivatives, with results for benzene in qualitative harmony with the earlier analytical treatment. The use of mechanical models to solve the secular equation of the molecular vibration problem is a very clever device of great promise, which, however, has not so far been very successful. The method suffers from several defects, the chief of which is the lack of flexibility since the springs representing the bonds must be taken out and replaced in order to change the force constants.

An analytical treatment<sup>78</sup> has been made of ammonia-type molecules, in which the most general quadratic potential function has been used. With the advent of deuterium compounds sufficient data are available in a few cases to utilize the general quadratic potential, with the result that the deficiencies of the simple valence-type or central-force type approximations are becoming increasingly apparent. Nevertheless, by using a two constant valence force treatment (the general function has six constants) a successful prediction<sup>69</sup> of the fundamental frequencies of  $\text{ND}_3$  was made, using the known data on  $\text{NH}_3$ . The same paper also discusses  $\text{PH}_3$  and  $\text{AsH}_3$ . In all analytical treatments made recently the full symmetry of the molecule has been used to factor the secular equation, usually by employing coordinates having the same symmetry as the normal coordinates. These coordinates may be obtained either intuitively or from group theory. A normal vibration treatment<sup>65</sup> of acetylene with one heavy hydrogen atom has been given and applied to the data.

A more accurate potential function for the inversion of the ammonia molecule was used to correlate the vibrational energy levels (belonging to the overtones of the symmetrical bending frequency) of  $\text{NH}_3$  and  $\text{ND}_3$ .<sup>74</sup> The dynamical problem of the energy levels of vibration and internal rotation for a four-carbon chain (such as in butane) having only valence forces has been approximately solved.<sup>72</sup>

The relation between the force constant and the interatomic distance has been refined<sup>63</sup> and extended to polyatomic molecules.<sup>64</sup> The potential energy function for diatomic molecules has been discussed in connection with known data.<sup>70</sup> Two papers dealing with the intensities of vibration-rotation bands of diatomic molecules have appeared.<sup>77, 78</sup>

The energy levels of a polyatomic molecule rotating in a crystal have been mathematically considered.<sup>76</sup>

**Dipole Moments.** A great many molecules have been subjected to dipole moment studies during the year. Of these, water,<sup>98</sup> deuterioammonia,<sup>86</sup> trimethylene chloride and 1,1,2,2-tetrachloroethane,<sup>96</sup> heptyl bromide, and butyl chloride<sup>95</sup> were measured as vapors, thus yielding dipole moments presumably more accurate than those from solution. The moment of water was found to be  $1.831 \pm 0.006 \times 10^{-18}$  e. s. u. The difficulty previously encountered of non-linear polarization vs. pressure curves was traced to adsorbed films on the insulation and largely eliminated. The moment of deuterioammonia was found to be  $0.03 \times 10^{-18}$  units higher than the value  $1.466 \times 10^{-18}$  redetermined for ordinary ammonia, possibly because the anharmonic character of the potential function governing the symmetrical bending vibration and the lower zero point energy of deuterioammonia cause the average value of the apex angle of the pyramid to be slightly smaller for deuterioammonia.

A very complete theoretical treatment of the temperature change of electric moment for molecules in which restricted "free" rotation occurs has been given,<sup>84</sup> including a calculation of the statistical weight function more rigorous than any previously published. This work was applied to the data for 1,2-dichloroethane and used to obtain the potential energy restricting free rotation, in the form of a two-term Fourier expansion.

The number of compounds investigated in solution is too large to list here but the papers involved are all included in the bibliography. It is becoming evident that measurements in solution do not often give the same value as measurements in the gas phase, the moments being ordinarily lower in the former case. Attempts to correct for the effect of the solvent by using empirical formulas involving the dielectric constant of the solvent sometimes, but not always, give good results. Important conclusions drawn from solution measurements are: the mercuric halides<sup>85</sup> have an appreciable moment, indicating that the molecule is not linear; the dielectric constant of solid nitromethane<sup>97</sup> is normal, suggesting that the molecule is not rotating in the solid; the presence of a triple bond raises the electric moment of the carboxyl group;<sup>103</sup> a triple bond also increases the moments of alcohols;<sup>101</sup> and the carbon valence angle is constant in compounds with two oxygens and either two hydrogens or an amyl and a methyl group attached to the same carbon.<sup>90</sup>

The anomalous dispersion of the large molecule lecithin in viscous mineral oils<sup>88</sup> has been studied with results not amenable to a simple treatment. The dielectric constant increments and apparent molal volumes have been determined for various betaines and *N*-dimethylantranilic acid.<sup>87</sup> Discussion of the results in terms of zwitterion theory was given. An extended study of the dielectric

and thermal changes in solid camphor at transition points has been published,<sup>104, 102</sup> together with a discussion based on the idea of rotation of molecules and groups in a crystal.

A rule<sup>100</sup> has been suggested for determining whether a substituent on a benzene ring will be *meta* or *ortho-para* directing; namely, "if the electric moment of a mono-substituted benzene derivative is greater than about 2.07 units, the next substituted group will be directed to the *meta* position, if less than 2.07 to the *ortho* and *para* positions."

**Magnetism.** Several papers concerning para- and diamagnetism are of importance in connection with valence theory. One<sup>110</sup> shows that the observed variations of the paramagnetism of salts of transition group elements can be explained equally well by the ideas of covalent bond formation, strong ionic fields, or by the use of molecular orbitals. Therefore, except that, empirically, covalent bond formation seems to have the strongest effect in quenching electron spin magnetic moment, the magnetic data do not distinguish between covalent and ionic bonds. Furthermore, predictions of structure [such as square  $\text{Ni}(\text{CN})_4^{--}$ ] can be made by any of these methods. The theory is applied quantitatively in another paper<sup>107</sup> to the data for  $\text{K}_3\text{Fe}(\text{CN})_6$  with results for the magnitudes, anisotropy and temperature dependence of susceptibility in good agreement with experiment. A computation<sup>105</sup> of the effect of the crystalline field on the susceptibility of samarium and europium ions enables the experimental data to be correlated with the theory. Measurements have been published<sup>108</sup> of the paramagnetic susceptibilities at several temperatures of a number of compounds of iron group elements and the results are compared with the theory wherever possible, with generally good agreement. Similar measurements for certain palladium compounds are given in another publication.<sup>109</sup> These latter were all found to be diamagnetic.

One draws the conclusion from these papers that the theory of the paramagnetism of solid compounds of transition group elements has been developed to a fairly satisfactory stage. The principal contribution to the susceptibility comes from the unpaired electrons but the orbital moment, though largely quenched, may contribute appreciably in certain cases. Measurements of magnetic properties may yield important information regarding the structure of the crystal in the immediate neighborhood of the magnetic atom.

Measurements on the diamagnetic susceptibility of the first five primary alkyl acetates and of methanol,<sup>113</sup> all as liquids, and of solid lithium hydride<sup>106</sup> have been published. In the first set, the susceptibility varies very little with temperature and Pascal's additivity law holds quite well. In lithium hydride the observed susceptibility is much less than that calculated by any of the rough methods for computing ionic susceptibilities. The author suggests

that the solid may possess a paramagnetism independent of temperature which decreases the apparent diamagnetism.

**Quantum Mechanics of Valence.** There are still three rather distinct approaches to the quantum-mechanical treatment of valence: (a) The only quantitatively reliable method is the use of the variation method with very complicated series-type variation functions, a procedure which has so far been applied only to the very simplest molecules, such as  $H_2$  and  $Li_2$ . The excellent quantitative results of such calculations are of great value but the enormous labor required has so far prevented their use for more complicated cases. During the year  $He_2^{+139}$ ,  $Li_2^{+116}$  and certain excited states of  $H_2^{133}$  have been so treated.

In an endeavor to obtain approximate results for much more complicated molecules, the method of atomic orbitals (b) and the method of molecular orbitals (c) are in vogue. The approximations introduced are of such an uncertain nature that both of these methods require empirical justification. Several papers have appeared giving various improved methods of handling the technical formalisms of the first of these procedures. These papers show the relation between the Van Vleck vector method and the bond eigenfunction method,<sup>114</sup> the method of expressing bond eigenfunctions in terms of a linearly independent set of functions,<sup>115</sup> the relation of the method of spin valence to that of Slater,<sup>140</sup> and a procedure for finding the number of structures of each degree of excitation for certain types of complicated molecules.<sup>141</sup> These are all highly technical papers with no bearing on the fundamental questions. A treatment<sup>135</sup> of hydrocarbon molecules, in which atomic orbitals, electron-pairing, and empirically determined integrals have been used, results in calculated energies agreeing to within a few tenths of a volt with the experimental values. The author concludes from his calculations that the principle of bond activity has no theoretical basis and does not hold, for example, in benzene. A consequence of this is that empirical resonance energies are of doubtful meaning, since they are based on bond additivity.

A long series of papers<sup>121-130</sup> on the use of the molecular orbital method to assign quantum numbers to the excited electronic states of polyatomic molecules has appeared. The ground states are also studied and ionization potentials, electroaffinity, and dipole moments discussed. A quantum-mechanical treatment<sup>142</sup> of the orientating power of substituents on the benzene ring was published, in which the electroaffinity of the substituent, resonance, and the polarizing influence of the reacting group were all considered in a rough semi-quantitative manner. A group theory discussion<sup>137</sup> of the molecular and atomic orbital methods sheds considerable light on the relation between these two approaches.

Two reviews of the problem of valence were produced during the year. One<sup>131</sup> is a survey of the classical background of elec-

tronic theories, leading up to a discussion of the Lewis theory, while the other<sup>138</sup> is a more mathematical discussion, dealing with the quantum-mechanical methods listed above. The latter will be found useful by any one wishing to learn the present day status of the problem, but it requires some quantum-mechanical background.

The quantum-mechanical treatment of solids, especially metals, received considerable attention during the year. Lithium,<sup>120</sup> copper,<sup>119</sup> and diamond<sup>118</sup> were treated by an approximate method in which solutions of the wave equation for each atom are obtained (using a Hartree field) obeying certain boundary conditions at the center of each face of a polyhedron surrounding the nucleus, these polyhedra fitting together to form the whole crystal. Lithium was also treated in a more accurate manner,<sup>134</sup> starting with Fock's equations (which include interchange) and proceeding to a higher approximation. The energy and interatomic distance so calculated agree well with experiment. The Thomas-Fermi statistical method was adapted to crystals<sup>136</sup> and modified to include interchange. The results are not accurate enough to give any stable interatomic distance but might serve as a starting point for the more exact treatments. The possibility that a solid metallic modification of hydrogen might exist under high pressures has been investigated theoretically,<sup>143</sup> with the conclusion that such a form probably is not realizable with available pressures.

Even the more approximate calculations of this sort on the solid state yield very interesting qualitative information, such as the nature of the difference between metals and non-metals, and promise results of great value in the future.

**The Allison Magneto-Optic Effect.** The status of the so-called magneto-optic method of analysis discovered by Allison over five years ago remains, to the outside observer, in an extremely unsatisfactory condition. If this effect is genuine, it ranks among the most important discoveries of its time, both for its possibilities of practical usefulness in a large number of directions and for its theoretical implications. If the effect is a result of experimental or psychological error, then there is indeed a very large body of data to be explained away. To the best of my knowledge there are six successful installations of this apparatus, in Auburn, Emory, St. Louis, Berkeley, Ames, and Urbana. The men who have operated these have made many tests, such as the analysis of difficult unknowns, which have convinced them of the reality of the effect. Nevertheless, a considerable number of observers have attempted to reproduce the experiment without success and some of these have expressed the opinion, based on their own experiences, that the minima of light intensity found are entirely psychological in nature.

If the effect is genuine, then it seems to be true that in its



present form it requires a very skilled operator. Furthermore, the conditions under which minima are observed do not seem to have been properly studied. Finally, practically no progress toward an explanation of the phenomenon has been made and little work seems to be in progress regarding this all-important problem. As a personal opinion, it would seem that a very great responsibility rests upon those who have succeeded in making this apparatus work; namely, to develop the equipment so that other investigators can reproduce the phenomenon and, perhaps by a publication of the results of tests of a really large number of unknowns, put an end to the doubts which exist concerning the reality of the method.

**Miscellaneous Topics.** An interesting paper<sup>155</sup> on the entropy of ice and other crystals having some randomness of atomic arrangement leads to certain conclusions regarding the positions of the hydrogen atoms in the lattice, including the idea that there exists a large number of possible configurations. A classical mechanical treatment<sup>150</sup> of the rotational entropy of molecules with freely rotating parts leads to formulas applicable to a number of cases. An extension of the methods for calculating thermodynamic quantities for polyatomic molecules from spectroscopic data has been made to the case in which degenerate frequencies occur.<sup>151</sup>

A new calculation<sup>153</sup> of the energy of the lowest state of the lithium atom, using a variation function which includes the distance between the electrons (Hylleraas type), gives a total energy in much better agreement with experiment than former computations but an ionization potential only slightly better (the old value having been quite accurate).

A thorough theoretical treatment of the van der Waals interaction of two hydrogen atoms has appeared.<sup>156</sup>

The polarizability of the hydrogen molecule has been computed,<sup>152</sup> using Wang's and Rosen's wave functions.

A rough wave mechanical treatment of the Mills-Nixon effect (the apparent stabilization of one of the Kekulé structures of benzene by certain substitutions) has been given.<sup>158</sup>

The Kerr constants for gaseous  $O_2$ ,  $N_2$ , and  $NH_3$  have been measured.<sup>149</sup>

Two papers dealing with the absorption spectra of crystals at low temperatures have appeared, the first<sup>157</sup> on the Zeeman effect with  $K_2Cr(SO_4)_2 \cdot 12H_2O$  and the other<sup>154</sup> on the spectrum of  $Eu_2(SO_4)_3 \cdot 8H_2O$ .

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## Chapter IV.

### Thermodynamics and Thermochemistry.

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Most of the articles containing the contributions to Chemical Thermodynamics and Thermochemistry published from American laboratories during the calendar year 1935 are listed by authors at the end of this chapter in such a way that the reader may have some idea of the nature of their contents. It will be seen that the output of work has been copious and so the space allotted is adequate only for very brief accounts of some of these papers. No attempt has been made to give a critical evaluation of the various publications and any apparent selection of topics has been dictated solely by the interests of the author.

Classical thermodynamics furnishes an invaluable system into which the facts of at least one-half of physical chemistry may be neatly fitted. The theory has long been complete, so that the advances in the subject go mainly along experimental lines. The sections of this chapter are, therefore, essentially classifications based on different types of experimental attack on physicochemical problems. Several papers have been published, however, on theoretical matters. Families of thermodynamic equations for poly-component homogeneous systems have been systematically studied and the group theory applied.<sup>6</sup> In this way the number of thermodynamic relations readily available has been greatly increased. Van Rysselberghe contributed several articles on technical points in the development of the subject,<sup>12, 13, 14</sup> including an attempt to develop a thermodynamics of irreversible changes. The temperature conditions for thermal equilibrium in a general gravitational field have been worked out by Tolman.<sup>11</sup> Several papers were written on the thermodynamics of explosions.<sup>1, 7, 8, 10</sup> Lewis and von Elbe<sup>8</sup> discussed the calculation and measurement of flame temperatures and decided against the presence of latent energy (highly excited molecules) in exploding gases. They<sup>7</sup> also used the thermodynamic functions computed from molecular constants to calculate theoretical explosion pressures for hydrogen and oxygen mixtures, with or without admixture of inert gases, and advanced hypotheses to account for the differences between the observed and calculated pressures. They noticed intense audible

vibrations during the explosions of lean mixtures, an effect which they explained by the time lag in the heat capacities of nitrogen and oxygen.

Bridgman<sup>3</sup> surveyed high pressure phenomena from a theoretical standpoint and also published a book on the thermodynamics of the electrical phenomena in metals.<sup>4</sup> The thermodynamics of magnetization incidental to low temperature measurement was outlined by Giauque and MacDougall.<sup>34</sup> Perhaps one of the most interesting contributions of the year was that of Bridgman<sup>2</sup> on the combined effects of high hydrostatic pressure and shearing stress on solids. A film of solid was compressed between a steel anvil and the circular face of a cylindrical piston. The anvil was rotated with respect to the piston, thereby applying a shear to the solid. While the paper is essentially experimental, it supplies excellent food for theory. The explosive decomposition of alums, silver nitrate, manganese dioxide, lead dioxide, celluloid and many other substances under these conditions, the curious transformations of organic substances, such as wood, rubber, bromothymol blue which becomes insoluble, open up an entirely new field in the chemistry of solids. These results are incidental, most of the paper being devoted to the polymorphism of elements under these conditions, and the changes produced in the tensile strength and other interesting properties.

The borderline field between thermodynamics and molecular mechanics has continued to yield results of advantage to both subjects. As a discussion of the details of these researches belongs in other chapters, only results will be given here. The heat capacity, entropy, free energy and dissociation constants of oxygen, calculated from molecular mechanics, have been revised to take account of the  $^1\Delta$  electronic state—the correction becomes important above 3000° K.<sup>23</sup> Values of the heat capacity of oxygen determined from ozone explosions, corrected for temperature gradients, agree well with these theoretically determined figures.<sup>59</sup> A very extensive compilation of the thermodynamic functions, including the dissociation constants, of gases (with full reference to sources) was published by Lewis and von Elbe.<sup>26</sup> New data for gases include the free energy of nitrous oxide, sulfur dioxide, hydrocyanic acid, and acetylene,<sup>21, 22</sup> Gordon having extended his method to include tetratomic collinear molecules; the thermodynamic functions of sulfur dioxide, carbon disulfide, and carbon oxysulfide, calculated from molecular constants, determined by electron diffraction, Raman and infra-red spectra; the free energy of formation of carbon disulfide and carbon oxysulfide and thermodynamic data for reactions involving hydrogen, sulfur, carbon, and oxygen;<sup>17, 18</sup> the thermodynamic functions from infra-red band spectra for hydrogen sulfide and its energy of dissociation into normal atoms;<sup>16</sup> the heat capacities of methane, methyl chloride,

methylene chloride, chloroform, and carbon tetrachloride over the range from 0 to 500° C., computed within 3 percent from Raman spectra data.<sup>28</sup> The entropy of nitrous oxide at its b.p. and at 298.1° K. and 1 atm. was computed from band spectra data<sup>44</sup> and compared with calorimetric data. The observed entropy is 1.14 units less than the calculated, a result which indicates that in the solid at low temperatures there is some lack of discrimination between the ends of the NNO molecule. Complete lack of discrimination between the ends would give a discrepancy of 1.38 E.U.

Ahlberg and Freed<sup>15</sup> give theoretical reasons for the assumption that the difference between the molal heat capacities of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  measures the electronic heat capacity of the latter salt. They have measured these heat capacities accurately from 17 to 295° K.<sup>15, 41</sup> and find good agreement between the experimental heat capacity differences and the calculated electronic heat capacity of  $\text{Sm}^{++}$ .

Significant information concerning the structures of crystals in which the possibility of randomness exists is obtainable from thermally measured entropies. The structure of ice has been made more definite in this way.<sup>27</sup> The lattice energies of alkali hydrosulfides were computed and found to be nearly the same as those of the corresponding bromides.<sup>29</sup> The results of Simon and Swain\* on the heat capacities of argon adsorbed on carbon were discussed with a view to throwing light on the mechanism of the binding of the adatoms.<sup>5</sup>

Fuoss and Kraus<sup>19, 20</sup> have continued their work on the computation of thermodynamic properties of solutions from molecular hypotheses, in particular the hypothesis of ion association, and Kirkwood<sup>25</sup> has made a significant contribution to the subject of solution thermodynamics by a discussion of the statistical mechanics of fluid mixtures.

**Temperature.** Details of the apparatus and method for cooling a system below 1° K. by the adiabatic demagnetization of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and for measuring the temperature were published from Giauque's laboratory<sup>33, 34</sup> during the year. A temperature scale from 12 to 273° K., in terms of a copper-constantan thermocouple, was determined by the helium thermometer and checked with the Leiden scale by hydrogen and oxygen vapor pressures. The results include a table of E.M.F.'s and temperatures from 12 to 90° K.<sup>31</sup> Four constant power series with the linear term omitted express the E.M.F.'s of these couples as a function of temperature from 2 to 90° K.<sup>30</sup> Observations of the variation with temperature of the refractive index of vitreous silica (determined by an interferometer method) were extended to -200° C. The results were applied to the calibration of vitreous

\* Simon, F., and Swain, R. C., *Z. physik. Chem.*, **B28**: 189 (1935).

silica refraction thermometers to  $-200^{\circ}\text{C}$ . Data for these thermometers over the range  $-200$  to  $1000^{\circ}\text{C}$ . are now available.<sup>32</sup> A long paper on the methods of testing thermocouples and materials<sup>37</sup> and another on chromel-alumel thermocouples<sup>38</sup> were published from the National Bureau of Standards. High-temperature work included an article on the emissivities at  $0.66\mu$  of cobalt, thorium, rhenium, and molybdenum between  $1300$  and  $2200^{\circ}\text{K}$ .<sup>40</sup> a sonic method for measuring the temperature in arcs,<sup>35, 38, 39</sup> and an exact discussion of the hot-wire method of measuring flame temperatures.<sup>8</sup>

**Thermal Measurements.** This section deals with those thermodynamic quantities which have been determined from thermal measurements; the results are arranged according to the types of compounds or reactions studied.

The heat capacities of solids up to high temperatures may be well represented<sup>45</sup> by an equation of the type  $C_p = a + bT + CT^{-1}$ . A combustible impurity present in tank oxygen, in amounts which vary with the pressure in the tank, may introduce an error into thermochemical measurements.<sup>55</sup> A new method is proposed for measuring the heats of evaporation of pure liquids by measuring the temperatures at two points in a vertical column of the liquid.<sup>47</sup> The heat capacity, heat of fusion, heat of evaporation and entropy of nitrous oxide up to its boiling point have been measured.<sup>44</sup> Heat capacities of strontium and barium oxides ( $55$ - $300^{\circ}\text{K}$ .),<sup>42</sup> of the two forms of tricalcium phosphate ( $15$ - $200^{\circ}\text{K}$ .),<sup>69</sup> and of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  ( $16$ - $300^{\circ}\text{K}$ .)<sup>41</sup> have been measured and the corresponding entropies computed. From experimental determinations of heats of solution in *N* sodium hydroxide and from vapor pressure measurements, Yost and Sherbourne<sup>72</sup> determined the heat of formation and free energy of formation of arsenous fluoride.

During the year much work was done on the thermal properties of hydrocarbons and petroleum products. Gaucher<sup>49</sup> examined all the available data on the heat capacities of hydrocarbons and petroleum products and gave an equation expressing  $C_p$  as a function only of the specific gravity, the boiling point and the temperature. It fits the data within 2 percent. Rossini<sup>66</sup> extended his very accurate work on heats of combustion at  $25^{\circ}$  to include isobutane ( $\Delta H = -686.31 \pm 0.13$  kcal per mole) and, by observing the regularities in heats of combustion of methane, mono-, di- and trimethylmethane, he estimated the heat of combustion and thence the heat of formation of tetramethylmethane (neopentane).<sup>65</sup> The adiabatic expansion principle combined with thermal expansions was used in the determination of  $C_p$  for butane and propane under temperatures and pressures where the systems were all liquid.<sup>67</sup> Measurements of  $C_p$  for the two-phase systems were made in an adiabatic calorimeter by observation of direct input of electrical energy.<sup>67</sup> Enthalpy-pressure-temperature diagrams ( $200$ - $800^{\circ}\text{F}$ . and up to  $1000$  lb./sq. in.) for pentane and benzene vapors have been made



and compared.<sup>60</sup> By the air flow evaporation method the heats of evaporation at 40° of 8 selected gasolenes were measured.<sup>54</sup> Pearce and Tanner<sup>63</sup> determined the heat capacity and energy of formation of naphthalene. Realizing the acute need for accurate thermochemical data for compounds of high molecular weight and recognizing the limitations in precision imposed on the heats of combustion of these compounds, Kistiakowsky<sup>56</sup> and his associates built a calorimeter for measuring the heats of catalytic hydrogenations and other reactions in the gas phase at temperatures not exceeding 150° C. Their precision was of the order of one per mille. With this apparatus<sup>57</sup> they determined at 355° K. the heats of hydrogenation of the following olefinic hydrocarbons: propylene, 1-butene, 2-butene (*trans*), 2-butene (*cis*), isobutene and ethylene. The heats for ethylene are also given at 298, 273, and 0° K. They observe that their results do not support the idea of constant bond energies but that the deviations from constant energies of bonding are in the same direction as Rossini found for the normal alcohols, increasing instability of the lower homologs.

The biologically important sulfur compounds, *l*-cysteine, *l*-cystine,  $\beta$ -thiolactic acid, and  $\beta,\beta'$ -dithiodilactic acid have been studied thermochemically with a new calorimeter. The heats of combustion at constant pressure at 25°, <sup>52</sup> and the heat capacities<sup>53</sup> from 90 to 298° K. were measured; from these data the entropies and standard free energies of formation were calculated. From the same laboratory<sup>70, 71</sup> the same kind of data and results for seven purine and pyrimidine derivatives were published. These results also throw light on the hypothesis of constant bond energies and indicate that, in the crystals at least, the bond energies are functions of the position of the bonds in the molecule.

Investigations of systems involving rubber hydrocarbon were published from the National Bureau of Standards. The heat of reaction<sup>61, 62</sup> of purified rubber with sulfur was measured at 175° C. and brought to 25° by observation of the heat content changes of the reactants over that range of temperature. The heat capacities<sup>43</sup> of crystalline and amorphous rubber hydrocarbon from 15 to 320° K. and its heat of fusion were measured and the entropies and the free energy of formation of the hydrocarbon computed.

In a study of the influence of impurities on physical properties, Skau measured the heats of fusion of an assortment of organic compounds.<sup>68</sup> The molecular heats of adsorption<sup>64</sup> of alkyl chlorides on charcoal change little from 25 to 50°; they increase with the size of the molecule, but are less with branched chains than with normal chains. Lamb and Ohl<sup>58</sup> used an ice calorimeter to measure heats of adsorption of a number of gases and vapors on chabasite, thomsonite, and brucite. The heats vary only slightly with the amount adsorbed and are considerably greater than those for the same gases adsorbed on charcoal. The heats of solution of some hydrazonium salts<sup>50, 51</sup> and the heat capacities of the solutions were measured.<sup>46, 51</sup>

Edsall<sup>48</sup> published data on the apparent molal heat capacities of aqueous solutions of amino acids.

**Volume-Pressure-Temperature-Concentration Relations.** The activity coefficients (fugacity/pressure) of 24 gases have been shown to be functions only of the reduced temperature,  $(T/T_c)$ , and the reduced pressure,  $(P/P_c)$ ,<sup>96</sup> over an extremely wide range of  $P$  and  $T$ . For helium, hydrogen, and neon  $(P_c+8)$  and  $(T_c+8)$  are used instead of  $P_c$  and  $T_c$ . This relation permits the prediction of activity coefficients for other gases with good approximation. It has also been applied<sup>110</sup> in the calculation of the effect of pressure and temperature on gaseous equilibria, and of the integral Joule-Thomson effect, and hence the change in enthalpy with pressure at constant temperature for many gases. The relation is not exact but does give results of very useful accuracy. Measurements of  $P$ - $V$ - $T$  relations at temperatures between 152 and 174° C. and from 1 to 8 atmospheres, on gaseous solutions of ethanol and water, indicate that the highest deviations from ideality are only 2 percent even at the highest pressures.<sup>86</sup> The critical constants of ethane<sup>74</sup> and propane<sup>75</sup> and  $P$ - $V$ - $T$  data for ethane<sup>74</sup> from 25 to 250° and up to 200 atmospheres have been determined with high precision. These data are well represented by the Beattie-Bridgeman equation, which even allows a long extrapolation to the critical point. Booth and his associates<sup>77</sup> determined the critical constants of seven fluoride gases and examined critical phenomena in the system  $\text{BF}_3$ -A.<sup>78</sup> These latter experiments have yielded very interesting results, retrograde condensation and a retrograde immiscibility at low temperatures and high pressures being observed.

Studies of the Joule-Thomson effect in gases include experimental determinations for nitrogen from -150 to 300° and from 1 to 200 atmospheres,<sup>99</sup> a correction by Deming and Deming<sup>83</sup> to previous calculations for this gas, and calculations<sup>98</sup> of the coefficient for nitrogen, methane, and their mixtures by the Beattie-Bridgeman equation over the range 200-400° K. and 1 to 100 atmospheres.

At room temperature and pressure a number of measurements of volume-concentration relations in liquid solutions were made, including the partial molal volumes of calcium and aluminum nitrates over the whole concentration range at 25°;<sup>154</sup> the apparent volumes of lithium chloride and bromide in aqueous solutions which, when plotted against concentration, give curves showing an incredible number of breaks;<sup>101</sup> the specific volumes of solutions of the chlorides of lanthanum, cerium, praseodymium, and neodymium;<sup>95</sup> the apparent volumes of betaines in water, alcohol, and benzene and in alcohol-water and alcohol-benzene mixtures;<sup>85</sup> and the apparent volumes of two zwitterionic substances giving tetrapoles in water.<sup>90</sup>

The compressibilities, fluidities, vapor pressures and surface ten-

sions of chloroform-methanol mixtures were measured and compared.<sup>82</sup> In the light of further measurements it was found that the modified Tait equation expressing the volume of an aqueous salt solution as a function of the pressure extrapolates very well, and the constant characteristic of the solution, viz., the effective pressure, is a linear function of the product of the concentrations of salt and water.<sup>88</sup> Gucker and Rubin<sup>91</sup> used the results of such extrapolations to compute the apparent molal isochoric heat capacities of six 1-1 electrolytes. Other measurements of compressions were made on aqueous solutions of lithium chloride and bromide,<sup>101</sup> methanol, resorcinol,<sup>89</sup> and three amino acids,<sup>81</sup> and on fractions of light midcontinent petroleum.<sup>84</sup> In these last two papers data are given to high pressures at different temperatures. The specific volume of pentane has been measured from 70 to 220° F. and up to 3000 lb./sq. in.<sup>100</sup> Wiebe and Tremearne<sup>103</sup> measured the volumes of liquid ammonia-hydrogen mixtures at 100° from 100 to 800 atmospheres, computed the partial volumes and discussed their thermodynamic significance. Bridgman<sup>79</sup> extended his measurements of the compressions and thermal expansions of lithium, sodium and potassium up to 20,000 kg/cm<sup>2</sup>. Interesting details of technique are given in this paper. He also found that impurities have very little effect on the compressibility of zinc,<sup>80</sup> and determined the compressibilities of a large number of intermetallic compounds.<sup>79a</sup> A careful study of the specific volume, thermal expansion and compressibility (10 to 85° and up to 800 atmospheres) of rubber-sulfur compounds was made by A. H. Scott.<sup>102</sup> The negative cubic coefficient of thermal expansion of solid silver iodide has been confirmed by careful experiment.<sup>94</sup> Expansion coefficients were also reported for single crystals of mercury,<sup>93</sup> 44 soda-alumina-silica glasses,<sup>87</sup> sodium tungstate,<sup>73</sup> and antimony.<sup>92</sup>

**Homogeneous Equilibria.** (a) *In gaseous systems.* Lewis and von Elbe<sup>26</sup> published an extensive compilation of dissociation equilibria in gases. They have also obtained the energies of the reactions  $\text{H}_2\text{O} = \text{H} + \text{OH}$  and  $\text{OH} = \text{H} + \text{O}$ .<sup>7</sup> The general equation for the activities of gases, already mentioned, enabled Newton and Dodge<sup>110</sup> to compute with useful approximation equilibrium constants of homogeneous gas reactions at higher pressures. Eastman and Ruben<sup>108</sup> have substantiated the work of Emmett and Schultz on the disturbing nature of the Soret effect on certain observations of equilibria in gas systems. The reaction,  $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$ , on which many equilibrium-constant measurements, all agreeing quite well, have been made, presents a problem which is troubling several sets of investigators. Statistical calculations, based on apparently irreproachable thermal data, do not give equilibrium constants which agree with those observed. Smith and Vaughan<sup>112</sup> made an American contribution to the problem, showing that the constants which they calculate are consistently one-half those observed

and they suspect the entropy of free rotation of ethane. By measuring the concentration of iodine photometrically, Cuthbertson and Kistiakowsky<sup>107</sup> determined the equilibrium constant of the decomposition of ethylene iodide between 50 and 125° C. and calculated the heat of dissociation. Equilibrium constants have been measured for the transformation of *cis*- to *trans*-dichloroethylene up to 975° by a flow method<sup>109</sup> and of the hydrogenation of pyridine to piperidine<sup>108</sup> around 160°. In both cases heat and free energy changes were computed. Calculations of the free energy of formation of benzoic acid from benzene and carbon dioxide at 522° K. lead to an equilibrium constant of the order  $10^{-7}$ . That benzoic acid actually is produced by such a reaction is laid to combination with the zinc catalyst.<sup>105</sup> Nies and Yost<sup>111</sup> obtained some thermodynamic constants for iodine trichloride by determining the equilibrium constants,  $P_{\text{ICl}}P_{\text{Cl}_2}$ , over the system  $\text{ICl}_3(s)$ ,  $\text{ICl}(l)$ ,  $\text{ICl}(g)$ ,  $\text{Cl}_2(g)$  at 25 and 35° and Barton and Yost<sup>104</sup> found that sulfur monochloride vapor did not decompose significantly at one atmosphere until the temperature reached 300°. The dissociation at lower pressures was studied between 160 and 800°.

(b) *Liquid Systems.* Chemical potential-concentration relations in zinc amalgams become ideal if the assumption is made that in the amalgam  $\text{Zn}_2$  and  $\text{Zn}_3$  are in equilibrium with  $\text{Zn}$ .<sup>120</sup> The first ionization constant of carbonic acid has been measured at 38° both by an E.M.F. method<sup>121</sup> and by a conductance method.<sup>124</sup> The results are, respectively,  $4.9 \times 10^{-7}$  and  $4.82 \times 10^{-7}$ . From Harned's laboratory there are reported measurements of the ionization constant of water in sodium chloride solutions<sup>117</sup> and the ionization constant of acetic acid in methanol-water mixtures.<sup>116</sup> In the latter case  $\log K$  varies as the reciprocal of the dielectric constant of the solvent. Ionization constants for  $\text{HSO}_4^-$ , calculated from kinetic data, agree well with those computed from conductance measurements.<sup>113</sup> The apparent dissociation constants of multivalent amino acids and peptides were determined in water solutions.<sup>115</sup> Walde<sup>125</sup> examined the significance of the first and second temperature derivatives of the logarithms of the ionization constants of weak electrolytes and found that  $\log K$  cannot be a quadratic function of the temperature. The classical dissociation constant of benzoic acid in aqueous salt solutions varies greatly with the nature of the salt.<sup>122</sup> Other papers report the fourth ionization constant of ferrocyanic acid,<sup>119</sup> the ferro-ferricyanide equilibrium data,<sup>118</sup> and a study of the equilibrium,  $\text{Fe}^{+++} + \text{Ag} \rightleftharpoons \text{Fe}^{++} + \text{Ag}^+$  in aqueous solution.<sup>123</sup>

**Heterogeneous Equilibria.** The heading of this section covers a multitude of topics and it seems convenient to split the descriptions into three classes: (1) systems of one component, including polymorphism and vapor pressures; (2) systems of two components, including most of the work on solutions; (3) systems of more than two components, under which sub-heading such things

as distribution coefficients and "salting out" effects naturally fall. All work on the thermodynamics of systems of isotopes and some of the E.M.F. measurements will be discussed in separate sections.

*Equilibria in Systems of One Component.* The outstanding advance in the thermodynamics of pure substances during the year was Bridgman's extension<sup>126</sup> of his observations on phase changes under pressure up to 50,000 kilograms per sq. cm., at least three times any former maximum working pressure. The vessel in which such pressures were generated was shaped like a truncated cone and, as the pressure inside was raised, this conical bomb was forced into a strong external sleeve so that a supporting pressure was applied to the outer wall. The pistons were made of a cemented alloy of tungsten and cobalt, carbonyl. With this apparatus new modifications of bismuth, mercury, thallium, tellurium, gallium, and iodine were found and their stability was examined. Above 20,000 kg./cm.<sup>2</sup> potassium chloride, bromide, and iodide invert, assuming possibly the cesium chloride type of structure. Goranson and Kracek<sup>132, 133</sup> studied the effect of pressures up to 1000 bars on the inversions and melting of sodium tungstate. The related thermodynamic quantities were calculated and the density of the solid was found to be 5.13, 20 percent higher than that given in the literature. Alumina inverts rapidly at 1300° when heated *in vacuo*; the temperature of the rapid inversion rises in atmospheres of hydrogen, air, and argon.<sup>130</sup> The importance of polymorphism and the frequency of its occurrence in organic compounds is steadily being realized; dimorphism (monotropy) was found in amyl bromide<sup>135</sup> and the solid-solid transitions in *d*-camphor, *dl*-camphor, *d*-camphoric anhydride, borneol, isoborneol, and bornyl chloride were studied intensively by examination of the effect of temperature on a wide variety of their physical properties.<sup>136, 137</sup> Vapor pressures of the following substances were measured: solid and liquid nitrous oxide<sup>44</sup> up to the boiling point, ethane<sup>74</sup> at 0 and 25° C., seven normally gaseous fluorides of group IV,<sup>77</sup> and barium by an effusion method.<sup>134</sup> Germann and Knight<sup>131</sup> published a book on vapor pressure-temperature charts. If methane and ethane are omitted, the boiling points of the normal paraffins may be expressed by the relation  $\log_{10} T_B (^\circ\text{K.}) = 1.07575 + 0.949128 \log m - 0.101 \log^2 m$ , where  $m$  is the molecular weight of the paraffin.<sup>129</sup>

*Equilibria in Systems of Two Components.* If  $f$  is any quantity that may be appropriately used in the well-known type of equation  $\frac{d \ln f}{dT} = \frac{\Delta H}{RT^2}$  (e.g., equilibrium constant, velocity constant, vapor pressure, etc.), Austin<sup>138</sup> has shown that, when  $\Delta H$  is either constant or varies linearly with

$T$ , a plausible approximation on integration gives  $\frac{f}{f} = \left( \frac{T'}{T} \right)^{\frac{\Delta H'}{RT'}}$ , where  $T'$  is any fixed standard temperature, e.g., melting point of pure solvent in a binary system. A similar approximation for equilibrium

constants was published by Douglas and Crockford.<sup>114</sup> With the help of this simplified equation, Austin calculated solubilities in certain simple eutectic systems and equilibria in binary systems involving solid solutions. He pointed out that simple consequences of the equation are the Ramsay-Young and Dühring rules. Simple semi-theoretical equations, expressing the chemical potential changes on mixing in binary systems in terms of the mole fraction, the volume fraction, and two parameters representing the departures from ideality, were evaluated by Scatchard and Hamer<sup>159</sup> from the mutual solubilities of several partially miscible substances and, hence, data on the liquid-vapor equilibria in the same systems were calculated, the results agreeing well with experiment. They also applied the same equations<sup>160</sup> to equilibria involving the solid and liquid solutions of silver-palladium and gold-platinum. Another paper giving a method for using data from one type of equilibrium in a given binary system to predict other equilibria in the same system is by Seltz.<sup>162</sup> He considers systems with complete liquid and solid miscibility and by a graphical method predicts the types of liquidus and solidus curves that correspond to different types of departures from Raoult's law in the solid and liquid solutions. The equation of Hildebrand and Wood\* for calculating solubilities from a knowledge of the properties of the pure components was tested by experiments on solutions of iodine, stannic iodide, sulfur and phosphorus. The results indicated that the equation was even more satisfactory than could have been expected from the approximations involved.<sup>147</sup> The temperature-solubility curves of helium in water between 0 and 75° at pressures up to 1000 atmospheres<sup>173</sup> show minima in the neighborhood of 30°. Measurements<sup>174</sup> also show that at 25° and up to 1000 atmospheres the solubility of a 3-1 hydrogen-nitrogen mixture in water may be calculated within a few percent from the solubilities of the pure constituents. Other measurements on liquid-gas equilibria (vapor pressures) were made on the following systems: calcium and aluminum nitrates in water at 25° over the whole range of concentration;<sup>154</sup> 10 and 20 percent solutions of methanol in water from 0 to 40°;<sup>211</sup> glycol-water, equations given for dependence of vapor pressure on temperature;<sup>169</sup> methane-crystal oil mixtures up to 50 percent methane, 70-220° F. and up to 150 atmospheres;<sup>158</sup> solutions of the halides and nitrate of ammonium in liquid ammonia at 25°, from which data activities and deviations from Raoult's law were computed;<sup>150</sup> ethanol-cyclohexane at 25°, positive departure from Raoult's law all the way;<sup>172</sup> pyridine-acetic acid (boiling points at one atmosphere);<sup>166</sup> and butanol-butyl acetate and butanol-acetone, in which systems the boiling points at one atmosphere were determined. Butanol and butyl acetate form an azeotropic mixture boiling at 116.50°.<sup>141</sup> Descriptions of apparatus for

\* Hildebrand, J. H., and Wood, S. E., *J. Chem. Phys.*, 1: 817 (1933).

the accurate determination of boiling points under reduced pressure,<sup>161</sup> and molecular weights by the ebullioscopic method<sup>151</sup> were published from the National Bureau of Standards.

An extremely interesting paper on solid-liquid-gas equilibria is that by Booth and Willson<sup>139</sup> on melting curves in the system boron trifluoride-argon. The curves indicate that six compounds ranging from  $A.BF_3$  to  $A.16BF_3$  are formed. Electronic considerations show that such compounds are possible. The dissociation pressures of these compounds are high, indicating considerable instability. The maxima and minima on the curves range between  $-127$  and  $-133^\circ C$ . At pressures above 35 atmospheres retrograde immiscibility was observed in this system.

In the course of an extensive program on the purification of organic compounds, Skau examined the systems (a) benzamide-*m*-nitrophenol, (b) acenaphthene-*m*-dinitrobenzene, (c)  $\beta$ -naphthylamine-*m*-dinitrobenzene,<sup>164</sup> and (d) acetanilide-propionanilide.<sup>165</sup> System (b) is practically ideal but a compound is formed; a new compound was discovered in system (d). The following systems depart almost insignificantly from ideality: *p*-dichlorobenzene-diphenyl, *p*-dichlorobenzene-naphthalene, and *p*-dichlorobenzene-triphenylmethane.<sup>152</sup> Ethylene dichloride forms a solid addition compound with ether (1-3, m.p.  $170^\circ K$ .) but not with benzene.<sup>149</sup>

During 1935 determinations were made of the solubilities of ammonium oxalate in water (0 to  $100^\circ$ , the monohydrate stable),<sup>148</sup> silver chloride in water,<sup>140</sup> mannose and other sugars in alcohols,<sup>170</sup> lead iodide in lead oxide,<sup>171</sup> and lead in mercury ( $20-70^\circ$ , results expressed by empirical equations).<sup>168</sup> From room temperature to  $575^\circ$  solid solutions ranging in composition from  $FeS$  to  $FeS_{1.14}$  appear from thermal analysis to exist in six forms, although such analysis does not show definitely whether the system remains homogeneous. The characters of the inversions from one form to another are modified by change in the sulfur content.<sup>156</sup> Draper<sup>146</sup> investigated the mineralizing action of  $HCl$  on the system  $MgO-Fe_2O_3$ . Further studies on hydrated alumina were reported.<sup>155</sup>

In a series of papers some aspects of the equilibria in the system  $Na_2O-B_2O_3$  were described<sup>142-145</sup>. The preparation of crystalline  $B_2O_3$  by dehydration of  $H_3BO_3$  *in vacuo* was announced; melting points of different compounds of  $Na_2O$  and  $B_2O_3$  and of  $K_2O$  and  $B_2O_3$  were given, together with the vapor pressures of  $B_2O_3$ ,  $Na_2O \cdot B_2O_3$  and  $Na_2O \cdot 2B_2O_3$ , determined by a dynamic method between  $1150$  and  $1400^\circ C$ .

*Equilibria in Systems of More Than Two Components.* Seltz<sup>198</sup> worked out the equations for the solidus and liquidus surfaces and the tie lines for solid-liquid equilibria in a ternary system where both the solid and liquid solutions are ideal. He points out that whereas the system copper-nickel is practically ideal, the system copper-nickel-gold is by no means ideal. Binary and ternary sys-

tems with biphenyl, bibenzyl and naphthalene approximate closely to ideal behavior.<sup>191</sup> Distribution coefficients of acetic acid between isopropyl ether and water,<sup>199</sup> of amino acids between butanol and water at 25°<sup>184</sup> and of hydrogen peroxide<sup>187</sup> between aqueous salt solutions and isoamyl alcohol or a mixture of acetophenone and carbon tetrachloride were determined. In the last case activity coefficients of hydrogen peroxide in the salt solutions were computed and lyotropic series observed. All the salts except sulfuric acid "salted in" the hydrogen peroxide.<sup>187</sup> Derivatives of amino acids which do not give zwitterions were prepared and their solubilities in water and alcohol studied.<sup>192</sup> The solubilities of nine salts in mixtures of methanol and water and of hydrogen peroxide and water were determined at 25°.<sup>177</sup> From the same laboratory were published data on the solubilities of helium and argon in many salt solutions.<sup>176</sup> The solubility of sodium bromide in acetone is increased by the presence of lithium or calcium perchlorate much more than the simple interionic attraction theory predicts.<sup>201</sup> An important and interesting paper by Schroeder, Gabriel, and Partridge<sup>197</sup> gives an account of the solubility curve of sodium sulfate between 150 and 350° C. and of the influence of sodium hydroxide and sodium chloride on this solubility. Below 300° C. addition of either of these substances decreases the solubility of sodium sulfate but above 300° it causes an increase, which in the case of sodium hydroxide is quite large and increases rapidly with the amount added. The following ternary systems involving water were studied over limited temperature ranges:  $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  (continuous solid solutions and many compounds, no congruent points);<sup>178</sup>  $\text{Na}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$  (0, 30 and 42°, alum found at the two higher temperatures);<sup>183</sup> cadmium acetate-acetic acid-water at 25° (complex addition compounds);<sup>181</sup>  $\text{CaSO}_4\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$  between 25 and 100°;<sup>189</sup>  $\text{Na}_2\text{SO}_4\text{-NaBrO}_3\text{-H}_2\text{O}$  (10, 25, 30 and 45°);<sup>196</sup>  $\text{NH}_4\text{Cl-NH}_4\text{NO}_3\text{-H}_2\text{O}$  (0.4, 25 and 50°, no complex salt, solid solution nor hydrate);<sup>194</sup> lithium phthalate-phthalic acid- $\text{H}_2\text{O}$  (0, 25 and 50°, compound formation);<sup>200</sup> allyl alcohol-salts- $\text{H}_2\text{O}$ ; <sup>186</sup> benzene-isopropyl alcohol-water (25°, ternary solubility diagram, distribution ratio, viscosity and refractive indices); <sup>193</sup> isoamyl alcohol-propyl alcohol-water (25°, solubilities, densities, and refractive indices).<sup>182</sup> Three very important contributions to the knowledge of equilibria at high temperatures were published during the year: the system  $\text{MgO-FeO-SiO}_2$  by Bowen and Schairer;<sup>179</sup> an exhaustive thermal, optical, and x-ray study of the system  $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{O}_3\text{-O}_2$ ;<sup>188</sup> and an investigation of the system  $\text{CaO-K}_2\text{O-Al}_2\text{O}_3$ .<sup>180</sup> Hydrothermal synthesis of clay minerals<sup>185</sup> and the phase changes occurring when kaolinite and dickite were heated were reported by Insley and Ewell.<sup>190</sup>

**Electromotive Force Measurements.** As usual, much has been published on electromotive force measurements. Although some



of this work had for its primary object the securing of thermodynamic data, much of it was directed towards theoretical studies on solutions and is more appropriately treated under that topic. Gross and Halpern<sup>207</sup> propounded a theory expressing normal electrode potentials in terms of one set of thermodynamic quantities characteristic of the solid phase only and another set characteristic of the solution. An investigation of the thermodynamics of the lead accumulator from 0 to 60° and over a wide range of acid concentration was made by Harned and Hamer. The results include determinations of the molal electrode potentials of the cells,<sup>208, 209</sup>  $\text{H}_2 \mid \text{H}_2\text{SO}_4(m) \mid \text{PbSO}_4 \mid \text{PbO}_2 \mid \text{Pt}$ , and  $\text{H}_2 \mid \text{H}_2\text{SO}_4(m) \mid \text{HgSO}_4 \mid \text{Hg}$ , under these conditions, computations of those thermodynamic properties which may be calculated from the chemical potential and its temperature derivatives, and quadratic equations<sup>210</sup> expressing the E.M.F. of lead accumulators over ranges of temperature and concentration. By fusion of AgO with AgBrO<sub>3</sub>, etc., on platinum wire, silver-silver halide electrodes yielding reproducible results in very dilute solutions were made and they were used in HBr solutions to 0.0001 molal<sup>213</sup> and in the determination<sup>221</sup> of the normal potential of the silver-silver iodide electrode from 5 to 40°. Cann and Mueller<sup>205</sup> determined the normal potential of the silver-silver chromate electrode and  $\Delta F^\circ$  for the reaction  $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{--}$ . Mercury-mercuric oxide-saturated barium hydroxide and calcium hydroxide electrodes were found to be easy to prepare, reproducible and constant.<sup>222</sup> Harned<sup>212</sup> measured the E.M.F. of cells  $\text{H}_2 \mid \text{HCl}(0.01), \text{NaCl}(m) \mid \text{AgCl} \mid \text{Ag}$  from 0 to 60°, computed results for other halide mixtures, and found further support for the linear variation of  $\log \gamma$  with molality at constant total ionic strength. He cast doubt on the validity of the empirical rules of Åkerlöf and Thomas, and extended Brönsted's theory of specific ionic interaction. The activity coefficients of sodium chloride in aqueous solutions were determined accurately from observations on cells with transference.<sup>204</sup> A considerable discrepancy was noticed between the observed and calculated E.M.F. of cells with a moving boundary between two electrolytes with a common ion; the cause was discussed.<sup>216</sup> Work has been continued on cells with solvents other than water: activities of sulfuric acid were determined in ethanol solutions with hydrogen and mercurous sulfate electrodes;<sup>223</sup> the molal electrode potentials of the silver-silver chloride electrode in 10 and 20 percent methanol-water solutions were determined from 0 to 40°, with the idea of examining the effect of the dielectric constant of the medium;<sup>211</sup> from measurements on cells of the type  $\text{Zn}(\text{amalgam}) \mid \text{ZnCl}_2 \cdot 6\text{NH}_3(s) \mid \text{NH}_4\text{Cl in NH}_3 \mid \text{CdCl}_2 \cdot 6\text{NH}_3(s) \mid \text{Cd}(\text{amalgam})$ , the thermodynamic constants,  $\Delta F^\circ$ ,  $\Delta H^\circ$ ,  $S^\circ$  at 25°, were calculated for the ammino cadmium chlorides and cadmium chloride. Provisional values for known potentials in terms of a stand-

ard hydrogen half cell in liquid ammonia were also given.<sup>206</sup> La Mer and Armbruster described a micro cell for use in heavy water investigations.<sup>215</sup> Some thermodynamic properties of solutions of straight chain sulfonic acids have been determined by a variety of experimental methods.<sup>217-220</sup>

**The Thermodynamics of Isotopes and their Compounds.** Assuming that the recombination of the gaseous atoms at the electrode is the rate-determining process in electrolyses where gases are produced, Halpern and Gross<sup>229</sup> derived a formula for the separation coefficients of hydrogen and deuterium in terms of their thermodynamic constants and their frequencies of thermal oscillation at the electrode. The formula limits the separation coefficient to approximately 11 to 13, which agrees with that found in the experiments of Brown and Daggett.<sup>227</sup> The differences between the vapor pressures<sup>127, 128</sup> of the 20.4° K. equilibrium mixture of deuterium (0.978 orthodeuterium) and of normal deuterium,  $\Delta P(e-n)$ , were measured from 15 to 20.4° K. and hence the difference between the vapor pressures of *ortho* and *para* deuterium was calculated and compared with values for *ortho* and *para* hydrogen.  $\Delta P(e-n)$  for deuterium is small compared with  $\Delta P(e-n)$  for hydrogen, but the ratios of these differences to the vapor pressures of the corresponding normal liquids are about the same. Heats of evaporation were computed and it was found that, in the absence of a catalyst, the vapor pressures of liquid normal deuterium changed less than one mm. of Hg in 200 hours whereas the vapor pressure of liquid normal hydrogen changed by one mm. in four hours. The results were discussed theoretically.

By a distillation method,<sup>236</sup> the ratios of the vapor pressures of  $H_2O^{16}$  and  $HDO^{16}$ , and of  $H_2O^{16}$  and  $H_2O^{18}$  were measured between 11.25 and 46.35° C. The vapor pressure of  $HDO^{16}$  is very nearly the geometric mean of the vapor pressures of water and deuterium oxide. Over the temperature range considered, the vapor pressure of  $H_2O^{16}$  is between 1.014 and 1.008 times that of  $H_2O^{18}$ . Hydrogen isotopes may be separated by the distillation of water, but the separation of oxygen isotopes by this method will be very difficult. From measurements of liquid-vapor equilibria, it was concluded that  $H_2O$ - $D_2O$  solutions are practically ideal.<sup>237</sup> Tables of the molar volumes of water and deuterium oxide from -20 to 95° C. and up to 12,000 kg./cm.<sup>2</sup>, and the transition parameters for the liquid and solid modifications between -60 and 20° C., up to 9000 kg./cm.<sup>2</sup> were published by Bridgman.<sup>226</sup> Unstable modifications, Ice IV, of both deuterium oxide and water were found in the field of stability of Ice V. In general, the molar volumes of deuterium oxide are always higher than those of water at the same pressure and temperature, and the equilibrium curves of deuterium oxide are always at higher temperatures. The broad differences in thermodynamic behavior may be ascribed to the greater zero point energy of water, but an expla-

nation of a detailed comparison of the results calls for some other considerations. The differences in zero point energy of protons and deuterons when attached to the anion or neutral water molecule lead to the conclusion that the ratio of the dissociation constants of acids in light and heavy water increases as the strength of the acid decreases.<sup>230</sup> Measurements with a quinhydrone electrode with hydrogen chloride in water and deuterium oxide gave the free energy of the reaction:  $2\text{DCl}(0.01m) + \text{QH}_2 = 2\text{HCl}(0.01m) + \text{QD}_2$  ( $\text{QH}_2 = \text{quinhydrone}$ ) and showed that the dissociation constant of  $\text{QH}_2$  in water is 3.84 times that of  $\text{QD}_2$  in deuterium oxide.<sup>231</sup> The absorption spectra and vapor pressures of hydrogen iodide and deuterium iodide<sup>224</sup> and hydrogen bromide and deuterium bromide<sup>225</sup> have been compared over a range of temperature for both solids and liquids. The vapor pressure of deuterium iodide is slightly greater than that of hydrogen iodide; indeed, the log of the vapor pressure of liquid deuterium iodide may be obtained by adding 0.01 to the calculated value of the log of the vapor pressure by hydrogen iodide. The vapor pressures of solid and liquid hydrogen and deuterium bromides are practically identical. It is interesting to note that the Trouton constants,  $\frac{\Delta H}{T_B}$ , for a number of isotopic compounds are not the same

for the hydrogen as for the corresponding deuterium compound. (The Hildebrand correction is insignificant.) In general, the isotopic change produces the greatest difference in the values of the constants for those substances which deviate most from Trouton's rule, e.g., water and ammonia.<sup>225</sup>

From spectroscopic data, Urey and Greiff<sup>234</sup> calculated equilibrium constants and enrichment factors for several exchange reactions involving isotopes of the lighter elements. A theoretical limit, which has been reached in some cases, is set to the precision of atomic weight determinations. Reactions for practical separations are suggested. The reaction  $\text{CH}_3\text{COCH}_3 + \text{DOH} \rightleftharpoons \text{CH}_3\text{COCH}_2\text{D} + \text{HOH}$  was studied between 35 and 80° C. in the presence of potassium carbonate. It is pseudo unimolecular with a high temperature coefficient of velocity and almost zero heat of reaction. The limiting equilibrium constant is 2.1 when corrected for the very disturbing formation of higher deuterioacetones.<sup>228</sup> Equilibrium constants for the reaction  $\text{C}_2\text{H}_2 + \text{HDO} = \text{C}_2\text{HD} + \text{H}_2\text{O}$  are as follows: 0.365 at 0°, 0.45 at 25° and 0.51 at 100°. <sup>232</sup> Most of the thermodynamic and other properties of deuterium determined before 1935 are summarized in a very exhaustive review article by Urey and Teal.<sup>235</sup>

**Miscellaneous.** A symposium on chemical thermodynamics was held at the San Francisco meeting of the American Chemical Society. Several papers on heat transfer and heat interchange largely from the industrial point of view were published during

the year.<sup>239, 240, 243</sup> The applications of thermodynamics to air conditioning<sup>238</sup> and to the problem of the swelling of wood<sup>241</sup> have also been discussed.

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## Chapter V.

### Contact Catalysis.

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The past year has been one of progress in the attack on the problems of the Mechanism of Contact Catalysis. Coupled with this work there have been marked advances in the theoretical as well as the experimental side of the kinetics of homogeneous gas reactions. The many studies on the kinetics of reactions, in which the wall of the reaction vessel acts either as a catalyst or an inhibitor, have their important bearing on the subject here discussed. However, since the subject of kinetics is fully taken up elsewhere in this volume only rarely will such work be considered in this Chapter.

Deuterium continues to be a valuable tool in the elucidation of the mechanism of catalytic reactions. Studies of the ortho-para hydrogen conversion on various catalyst surfaces have made additional contributions to our knowledge of the mechanism of contact catalysis. An important contribution not only to the subject of catalysis but also to the whole field of chemistry has been made by Kistiakowsky<sup>31, 32</sup> and his coworkers. These investigators made remarkably careful and accurate determinations of the heats of reaction resulting from the catalytic hydrogenation of ethylene and other simple olefinic hydrocarbons. By using a flow system they were able to eliminate the problem presented by the adsorption of the gases by the catalyst. The heats of reaction differ somewhat from the present values which are obtained from heats of combustion. Such differences are likely to raise many questions in theoretical chemistry. The results so far reported do not bear out the theory of constant bonding energies.

Again it seems best to divide the work into two general groups. Accordingly, the work which primarily concerns the "Mechanism of Contact Catalysis" will be considered first and this will be followed by a consideration of "Catalytic Reactions." The terms "activated adsorption" and "chemisorption" will again be used as equivalent expressions. It is to be regretted that important foreign contributions as well as many interesting points and suggestions by American investigators have had to be omitted from this survey.



## MECHANISM OF CONTACT CATALYSIS

Use of the rate equation in studying a number of heterogeneous reactions has led to an apparent relationship of  $A = C_0 e^{OE}$ , where  $A$  is the activity constant of the reaction,  $E$ , the energy of activation and  $C_0$  and  $c$  are constants. In a theoretical consideration of problems of activity and activation energy in heterogeneous gas reactions, Storch<sup>47</sup> found that changes in the frequency of energy transfer between the adsorbed gas and the surface was an important factor in determining the above relationship. Frequency of the energy exchange in the adsorbed phase may be reduced markedly when multiple adsorption occurs and hence be a function of the spacing of catalyst atoms. It was shown that the above relationship could not be due entirely to a probability distribution of the active centers. In hydrogenations it did not seem necessary to postulate a hydrogen atom leakage through an energy barrier.

The use of deuterium continued to lead to further insight into the mechanism of surface action. Morikawa, Benedict and Taylor<sup>39</sup> studied the exchange between deuterium and methane on the surface of reduced nickel catalysts in the temperature range up to 305°. At the upper temperature, equilibrium on the heavy methane side was established in twenty hours. At 218° the equilibrium was reached in fifty hours. At 110° no exchange was detected in ninety hours. Exchange was found to occur at as low a temperature as 170°, which was taken as evidence for the activated adsorption of methane at this temperature. This is at least 200° lower than the temperature at which the usual methods of adsorption reveal any activated adsorption of methane on nickel. These same authors<sup>51</sup> used deuterium to study the activation of specific bonds in complex molecules. Deuterium or hydrogen was adsorbed under such conditions that it was present in an activated form. It was possible to determine the conditions under which exchange of deuterium with ethane occurred without any appreciable amount of ethane having reacted with the deuterium (or hydrogen) to form two molecules of methane. At 138° exchange proceeded quantitatively, while the production of methane set in at 150° and was sensibly complete at 200°. Since the exchange reaction involved only the C-H bond, while methane production involved the C-C bond, the different conditions of reaction, temperature, and catalyst, were obtained for the activated adsorption of ethane molecules producing either a C-H or a C-C bond split. This work will no doubt have important consequences in the study of the catalytic behavior of saturated hydrocarbons and the activation of specific chemical bonds in the more complex molecules.

Further studies have been conducted on the catalytic exchange reaction between water and deuterium. Taylor and Diamond<sup>48</sup> found a rapid exchange between deuterium gas and the water retained by such catalytic materials as chromic oxide, zinc oxide, zinc chromite, alumina, and platinized asbestos. The reverse action between hydrogen

and heavy water on the surface was demonstrated. The mechanism of the reaction was considered to be due to the activated adsorption of hydrogen (or deuterium) on the chromic oxide, zinc oxide, and zinc chromite, while the water was adsorbed in an activated state by the alumina. The existence of this exchange is important, since it may cause unintentional replacement of deuterium by hydrogen in reaction mixtures. At room temperature Taylor and Jungers<sup>50</sup> obtained an exchange between ammonia gas and deuterium over an iron synthetic ammonia catalyst. Activated adsorption of both ammonia and deuterium must take place in order for the exchange to occur; since at higher temperatures these reactions would proceed rapidly, they cannot be the rate-determining steps in the ammonia synthesis. The activated adsorption of nitrogen probably is the rate-determining step. Such studies as these indicate the delicacy of isotopic chemistry in revealing the nature of the association between surface adsorbent and adsorbate. In this latter case activated adsorption of ammonia is shown to exist at temperatures where the usual methods could not distinguish between van der Waal's and activated adsorption.

Additional studies on the effectiveness of catalysts in ortho-para hydrogen conversion have given further information on the nature of the catalyst surface and the types of adsorption. Emmett and Harkness,<sup>15</sup> using iron, nickel, and platinum as catalysts, observed the effect of the previous treatments of the catalysts on the ortho-para conversion at  $-190^{\circ}$ . A catalyst outgassed at  $450^{\circ}$  and cooled to  $-190^{\circ}$  in helium gas was ten to twenty times as effective as a catalyst cooled in hydrogen gas. The iron catalyst could be run indefinitely at  $-190^{\circ}$  with no poisoning effect due to adsorbed hydrogen, while the nickel catalyst lost activity at this temperature. Nitrogen added to the iron catalyst reduced its activity when used at  $100^{\circ}$  and  $450^{\circ}$ . Adding nitrogen at  $-190^{\circ}$  to the iron catalyst which had been cooled in hydrogen reduced its activity seventy percent. The adsorbed nitrogen could be rather well removed by warming in hydrogen to room temperature. The platinized asbestos lost activity at  $130^{\circ}$  on being exposed to hydrogen at atmospheric pressure. The poisoning of these catalysts by the various gases was attributed to their activated adsorption. These results support strongly the concept that activated adsorption is a surface phenomenon. In this investigation, as well as in their study of the adsorption of hydrogen by iron synthetic ammonia catalysts, Emmett and Harkness<sup>16</sup> obtained additional evidence for the existence of at least two kinds of activated adsorption of hydrogen. The first type occurred at a convenient rate at  $-90^{\circ}$  and above, while the second kind was found at  $100^{\circ}$  and above. Both types were largely surface adsorptions rather than activated diffusion. The ortho-para and the para-ortho conversion of hydrogen was also used by Taylor and Diamond<sup>49</sup> to determine the effectiveness of sixteen different paramagnetic and diamagnetic surfaces. Paramagnetic gadolinium and neodymium oxides caused rapid conversion, while diamagnetic lanthanum oxide had

an effectiveness that was several orders lower. For comparable surfaces paramagnetic substances showed greater effectiveness than diamagnetic surfaces for similar van der Waal's adsorptions. Paramagnetic surface atoms must exist on diamagnetic bulk copper and silver in order to explain their catalytic effect or else residual activated adsorption may be present. High temperature activated adsorption was found to be effective in the para-ortho conversion at higher than liquid air temperatures. A new high temperature conversion was found on an alumina surface which seemed to indicate a possible exchange mechanism with the water adsorbed in an activated state.

Evidence, supporting the concept that hydrogen may be adsorbed in different ways by the same metal surface, depending upon the temperature, was obtained by Rowley and Evans<sup>43</sup> in their measurements of the accommodation coefficient of hydrogen on iron. If the surface of the metal remained unchanged, the accommodation coefficient should fall with falling temperature. These investigators found, instead, a greater rise in the coefficient than they had previously observed in the case of platinum and tungsten wires. They attributed this to a greater adsorption of hydrogen and offered the explanation that above 500° K. the surface of the iron was uniformly covered by activated hydrogen (probably atomic). Below 500° K. a second type of more loosely bound gas was present on the surface and below 350° K. a molecular type of adsorption predominated. When special techniques were used to remove the adsorbed hydrogen, the values of the coefficient always dropped. Cashman and Huxford<sup>7</sup> studied the photoelectric properties of magnesium in the presence of traces of hydrogen and oxygen. Chemisorbed layers of hydrogen and oxygen were considered to produce single layers of MgH and MgO on the surface. These layers produced shifts in the photoelectric threshold of magnesium. A second shift in this threshold was found when more hydrogen was added; this was attributed to induced dipoles in weakly adsorbed hydrogen molecules. Additional oxygen desensitized the magnesium, probably as a result of the formation of a thicker magnesium oxide coating. Mixed hydrogen and oxygen, present in traces, markedly sensitized magnesium and this was thought to be due to the formation of a single layer of MgOH.

Copper catalysts, poisoned to varying degrees by oxygen, were used by Russell and Ghering<sup>44</sup> in the hydrogenation of ethylene at 0° for the purpose of studying the nature of the copper surface. The surfaces showed extreme sensitivity to variations in the method of preparation. Copper poisoned at 0° by oxygen showed a slow removal of the oxygen at 20° by the hydrogen-ethylene mixture but no removal was observed at 0°. Catalytic activity toward the hydrogenation of ethylene disappeared completely when the surface was only 40 percent saturated with oxygen. Calorimetric measurements were obtained for the heat of adsorption of oxygen by these catalysts. These results indicated that the direct sorption of oxygen was largely non-preferential, so that the heats of adsorption gave no indication of the catalytic behavior of

the surface. However, successive removal of small amounts of the adsorbed oxygen by reduction with hydrogen showed that the least active part of the surface was released first. Nitrous oxide was also used as a poison and interesting results were obtained in this case. The decomposition of the nitrous oxide on the copper surface proceeded with no increase in pressure up to a temperature of  $75^{\circ}$ . Thus, the oxygen of the nitrous oxide was adsorbed while the nitrogen was given off. Decomposition occurred at as low a temperature as  $-78^{\circ}$ . Considerable oxygen was taken up from the nitrous oxide before any poisoning resulted. The catalyst could be completely poisoned for the nitrous oxide decomposition by the adsorption of oxygen and still be catalytically active enough to cause some hydrogenation of ethylene. A more active surface thus was needed for the decomposition of nitrous oxide than for the hydrogenation of ethylene. The evidence in the main supported the point of view that the investigators were dealing with a non-uniform surface of copper. A large part of the surface was not catalytically active. The most active portion of the surface was probably inactive in the hydrogenation of ethylene at  $0^{\circ}$ , due to the adsorption of ethylene itself as a poison. According to Griffin<sup>20</sup> a supported copper catalyst which had been poisoned by a trace of carbon monoxide showed an increased capacity to adsorb hydrogen at all pressures up to one atmosphere. A larger amount of carbon monoxide caused a low pressure increase in the adsorption of hydrogen but a decrease at higher pressures. The traces of carbon monoxide seemed to be adsorbed on the most active centers and aided in binding more hydrogen, while the larger amounts were adsorbed on the less active centers to the exclusion of equivalent amounts of hydrogen. In spite of these recent contributions to the problem, the mechanism, or perhaps one should say the mechanisms, of the different types of activated adsorption still remains in doubt.

**Adsorption of Gases.** Several papers have appeared concerning the adsorption of gases by solids which are related to catalysis either directly or indirectly. Cunningham<sup>9</sup> has extended the Langmuir theory by considering that a gas molecule need only come within a certain range of attraction of the surface to be adsorbed. The theory leads to the conclusion that surfaces may have several kinds of elementary spaces and gives a method for determining their number. For the examples used the mathematical treatment is in good agreement. Herzfeld<sup>23</sup> considered the speed of condensation and sublimation from the surfaces of solids. The formula for the equilibrium pressure was found to be changed in the case of the condensation and sublimation of atoms if the electron weight in the gaseous state is different from the solid state. For true metals the speed of sublimation is probably increased, while for non-metals a reflection coefficient exists. The equilibrium pressure for molecules comes out to be higher than for atoms because in sublimation there is a transition from limited oscillation of the axes to free

rotation which tends to increase the speed of sublimation. Lamb and Ohl<sup>34</sup> measured the heats of adsorption of a number of gases and vapors on dehydrated chabasite, thomsonite, and brucite. Molar heats of adsorption of those substances copiously adsorbed were found to be somewhat larger than those previously observed for charcoal and silica gel but, like them, they varied only slightly with the amount adsorbed. These crystalline substances seemed to exert more intense adsorptive and compressive forces on the gases and vapors studied than does charcoal. Polanyi's potential theory was applied to the van der Waals' adsorption of argon and nitrogen on iron synthetic ammonia catalysts at liquid air temperatures by Emmett and Brunauer.<sup>14</sup> The results fitted the Polanyi theory very well. The early part of the potential curves represented the building of monomolecular layers, the straight line section indicated the formation of multimolecular layers, while the high pressure part pointed to condensation of the gas in capillaries of the adsorbent. Thus Polanyi's theory is not limited to multimolecular layers of adsorbate but in this case, at least, it applies to monomolecular layers and capillary condensation as well. Brunauer and Emmett<sup>6</sup> determined the van der Waals' adsorption of such gases as nitrogen, oxygen, and argon by iron synthetic ammonia catalysts for the purpose of estimating the surface area of these catalysts. By extrapolating the linear portion of the isotherms back to zero pressure and assuming close packing, they calculated the mean value of the surface area to be 17.6 square meters for a 46 gram sample, if the molecular diameters are taken from the densities of the solidified gases, and 20.6 square meters if the diameters are obtained from the densities of the liquefied gases.

Rather unusual results were found by Beebe and his coworkers<sup>2</sup> when they measured the adsorption of hydrogen and deuterium on copper at pressures from zero to two mm. At  $-78^{\circ}$  the rate of adsorption of deuterium was less than for hydrogen but equal amounts of the two isotopes were adsorbed at equilibrium. It was concluded that activated adsorption occurred at this temperature. In the temperature interval 0 to  $125^{\circ}$ , the rates at which the two isotopes are adsorbed underwent an inversion, deuterium being more rapidly adsorbed at the higher temperature. Direct calorimetric measurements of the differential heats of adsorption of the two isotopes showed them to be identical within the limits of experimental error. The early rate of adsorption at  $-78^{\circ}$  was autocatalytic.

**Surface Properties and the Preparation of Catalysts.** Copley and Phipps<sup>8</sup> directed a constant molecular beam of potassium iodide against a heated tungsten filament and studied the positive ion current obtained. The tungsten filament was first oxygen coated and later stripped of this gas by flashing at high temperatures. In the region of a stable oxygen layer the positive ion current was

constant and higher than after the wire was flashed. The current decreased with increasing temperature. This behavior was the same as found when a beam of potassium atoms was used, which indicated that the ionization process was the same in both cases. Preliminary dissociation of the adsorbed salt into atoms must first occur. Positive ions were found by Kunsman and Nelson<sup>33</sup> to be emitted from an iron potassium catalyst for ammonia synthesis after the catalyst had become inactive as a clean up agent, indicating that metal surfaces emitting positive ions were not necessarily good catalysts.

A new method was worked out by DuMond and Youtz,<sup>12</sup> whereby gold atoms could be successively laid down in step-wise layers of twenty atoms thick. They then measured the selective x-ray reflection from these stratified metal films whose thickness was 10,000 Å. Diffraction maxima, whose intensity falls off exponentially with the time, were obtained from this grating. The half life of the surface was from two to three days. If this technique could be applied to the study of the surface of metal catalysts, it might provide a means of studying intimately the diffusion of atoms in the solid state.

A new way to prepare finely divided metals was developed by Insley,<sup>24</sup> who carefully distilled the mercury from amalgams of these metals. Copper, iron, cobalt, and nickel, prepared in this way, were neither as good adsorbents for hydrogen, ethylene, or ethane, nor were they as good catalysts in the hydrogenation of ethylene as the same metals obtained in a fine state of division by reduction of the oxides. The results indicated a small amount of van der Waal's adsorption of hydrogen by the nickel prepared from the nickel amalgam and a somewhat larger activated adsorption. However, it was not proved that the last traces of mercury were completely eliminated by the process and any such traces might well act as poisons. Baldeschwieler and Mikeska<sup>1</sup> were able to prove that the poisons and impurities on spent platinum catalysts must be eliminated before the material could be made into an effective platinum oxide catalyst once more. Recommended procedures were not successful in doing this and modifications were worked out. Conversion to chloroplatinic acid and precipitation by ammonium chloride under controlled conditions enabled them to prepare a catalyst of high activity. The effectiveness of various zinc oxide-chromium oxide catalysts in the methanol synthesis was made the basis of a study by Molstad and Dodge.<sup>38</sup> Short time tests indicated the best ratio to be  $\text{Zn}_{75}\text{Cr}_{25}$  but it was found that catalysts of higher chromium content increased in activity with use coupled with operation at temperatures above maximum activity. The composition of the catalyst, having maximum activity, was finally located at  $\text{Zn}_{50}\text{Cr}_{50}$ . This catalyst was rugged, produced nearly pure methanol, and appeared to be uninjured by long use. Such

complete studies as this show how futile it is to decide on the composition and behavior of a catalyst before full information is available.

**Heterogeneous Reaction Kinetics.** In order to evaluate more satisfactorily the kinetics of reactions of the type  $A(s) = B(s) + C(g)$ , Benton and Cunningham<sup>3</sup> studied the rate of thermal decomposition of light sensitive silver oxalate, on which nuclei had been previously produced by irradiation. Exposure to light, especially to  $\lambda\lambda < 520 \text{ m}\mu$ , greatly increased the rate of the subsequent thermal reaction. Oxygen present during exposure resulted in marked initial poisoning as compared to exposure in nitrogen and carbon dioxide. Long exposure to light resulted in slight decomposition of the oxalate. Exposure to light produced a greater effect in the lower decomposition temperature range than it did in the higher range. The increased yield over unexposed samples was roughly proportional to the number of quanta absorbed for short exposures but long exposures were relatively less effective. The theoretical treatment, based on simple assumptions regarding nuclei formation and their subsequent growth, was found to be in reasonably good agreement with the early stages of decomposition. Activation energy of nucleation was found to be about 64 K. cal., while that for growth of nuclei was 8.5 K. cal.

The decomposition of deuteroammonia on tungsten wires at about 950° K. was observed to be approximately of zero order by Jungers and Taylor<sup>30</sup> in the pressure range of 3.5 cm. to 15 cm. The surface area was nearly saturated but the zero order decomposition was slower than for ammonia under the same conditions. The temperature coefficient of decomposition was the same for the two ammonias. Zero point energy differences are able to account for the differences in the decomposition velocities. Pease and Wheeler<sup>41</sup> used a copper catalyst and measured the rate of hydrogenation of ethylene by hydrogen and deuterium at 0°. The results indicated a ratio of rates of  $\text{H}_2/\text{D}_2 = 1.59$ . At higher temperatures this ratio fell but the possibility of exchange was not excluded. The exchange reaction between benzene and heavy water was found by Bowman, Benedict and Taylor<sup>4</sup> to proceed slowly over a nickel catalyst at 200° in a closed system. Finally, all of the hydrogen atoms of benzene were found to be replaced by deuterium resulting in the formation of benzene  $\text{d}_6$ .

A smooth platinum wire was used by Dixon and Vance<sup>11</sup> in their study of the reaction between hydrogen and nitrous oxide at 260 to 471°. The reaction was nearly independent of the hydrogen pressure and approximately proportional to the nitrous oxide pressure, indicating that reaction occurred when nitrous oxide molecules with an activation energy of 23,100 cal. collided with surfaces which were practically covered with hydrogen. Jackson<sup>29</sup> placed tungsten or platinum as a catalyst in the gas stream, coming from

an electrical discharge through water vapor, to remove atomic hydrogen. This gas stream with 80 percent of the atomic hydrogen removed was about 90 percent as effective in the oxidation of carbon monoxide. Possible chain reactions, involving OH radicals or hydrogen peroxide, were suggested as mechanisms for this reaction. In the slow oxidation of propane, Pease<sup>40</sup> had to use a glass tube poisoned by potassium chloride, because the reaction was strongly inhibited by the glass surface. Heisig and Wilson<sup>22</sup> found that the action of bromine on butadiene was a surface reaction, occurring rapidly on glass surfaces as catalysts. Adsorption of the product on the glass slows down the action to a constant rate.

#### CATALYTIC REACTIONS.

**Hydrogenation.** Carbon dioxide was hydrogenated to formic acid over Raney nickel catalysts at 80° or less in the presence of amines as reported by Farlow and Adkins.<sup>17</sup> Sheet brass was effective as a catalyst at 250°. Formates were formed but, if the reaction was carried out at much above 100°, the formate of the amine was dehydrated to the substituted formamide. Using platonic oxide as a catalyst, Glattfeld and Schimpff<sup>18</sup> observed that the delta-lactones of aldonic acids were reduced to the corresponding sugars. Gamma-lactones were also reduced but the sugar yields were usually lower, due to the further reduction to the corresponding sugar alcohols. Both platonic oxide and Raney nickel were used by Lutz and Palmer<sup>35</sup> in the hydrogenation of 1,4-diketones. *trans*-Dibenzoylethylene may under different conditions give both mono and dimolecular products, while other 1,4-diketones, including *cis*-dibenzoylethylene and the halogen derivatives, underwent largely monomolecular reduction. The formation of furous and cyclic dimolecular products suggested that in these cases catalytic hydrogenation involved conjugate addition. Stevinson and Hamilton,<sup>46</sup> using Raney nickel, were able to catalytically reduce nitro-arylarsonic acids to amino-arylarsonic acids without affecting the arsono group. Raney nickel catalysts were also found by Van Duzee and Adkins<sup>53</sup> to be effective in the hydrogenation and hydrogenolysis of a series of ethers. Hydrogenolysis occurred in some cases at temperatures lower than necessary for hydrogenation.

**Oxidation.** The rate of burning or the disappearance of a carbon film from glass surfaces or from glass coated with chlorides of the alkalis, chlorides and hydroxides of the alkaline earth metals or the sulfates of sodium and potassium, was made the basis of a study by Day, Robey, and Dauben.<sup>10</sup> The salts markedly speeded up the disappearance of the carbon film at temperatures of 515 to 575°. The salt surfaces probably acted as catalysts in the decomposition of surface complexes of the type  $C_xO_y$ . This was previously suggested by Taylor and Neville for the effect of salts on the reaction



of steam upon carbon. By an improved technique Milas and Walsh<sup>37</sup> oxidized furane, furfural, furfural alcohol, and furoic acid over such catalysts as vanadium pentoxide, bismuth vanadate, and a ten percent molybdenum oxide, ninety percent vanadium pentoxide. Maleic acid was found to be the chief solid product. Walker and Christensen<sup>54</sup> accomplished the quantitative oxidation of methane by passing it twice over mixed oxides of cobalt and copper on unglazed porcelain at a rate of 20 to 25 cc. per minute over 3.5 g. of catalyst at 550°, provided the ratio of oxygen to methane was at least three to one.

**Miscellaneous Reactions.** Several interesting investigations have appeared which involve alkylation and polymerization. Direct alkylation of aromatic hydrocarbons was achieved by Malishev,<sup>86</sup> who used phosphorus pentoxide, mixed with cresol peptized lamp-black, as a dispersion catalyst in the hydrocarbons. At temperatures of 200° to 250° under pressures up to 40 atmospheres, ethylene added to benzene to form mono- and hexaethylbenzene, isobutylene added to benzene to form *tert*-butylbenzene, propylene added to toluene (at 150°) to form *p*-cymene and naphthalene was ethylated by ethylene. Grosse and Ipatieff<sup>21</sup> obtained what was termed destructive alkylation when a paraffin hydrocarbon in the presence of  $\text{AlCl}_3$  or  $\text{ZrCl}_4$  at 50-75° split into a lower hydrocarbon and an olefin which immediately reacted with an aromatic hydrocarbon to alkylate it. Ipatieff and Grosse<sup>27</sup> further found that different classes of hydrocarbons, i. e., paraffins, naphthenes, aromatics and olefins, reacted with ease among themselves in the presence of catalysts. The halides of a number of the elements proved to be effective but boron fluoride in the presence of finely divided nickel and either water or anhydrous hydrogen fluoride was studied most completely in the cases of reactions between paraffins and olefins. The paraffins so far alkylated gave higher weight molecules through addition of one, two or more molecules of olefin—and they all contained a tertiary carbon atom. Together with his coworkers, Ipatieff<sup>25, 26, 28</sup> has followed the polymerization of gaseous olefins under high pressure in the presence of phosphoric acid. Ethylene yielded a mixture of paraffinic, olefinic, naphthenic and aromatic hydrocarbons. Propylene polymerized to a mixture of mono-olefins and isomeric butylenes at atmospheric pressure and relatively low temperature formed liquid polymers which proved to be mono-olefins.

Using copper-silica gel and copper chloride-silica gel catalysts, Reyerson and Yuster<sup>42</sup> followed the chlorination of propane over a temperature range from about 50 to 275°. In the presence of the catalysts the heat of activation was about half of that for the homogeneous reaction and the extent of chlorination was greater at a given temperature. A new type of hysteresis was observed when the partial pressure of chlorine was half an atmosphere or over.

When, and only when, the reaction was carried to a temperature such that there was a 100 percent chlorination was the hysteresis effect found. If the temperature of the catalyst chamber was lowered as much as 60 to 80°, the chlorination persisted at 100 percent, instead of dropping as it had in the homogeneous reaction. This catalytic hysteresis made it possible to study the pyrolysis of the propyl chlorides which was found to take place. A coupling reaction was also shown to be present. Anhydrous zinc chloride was the catalyst used by Underwood and Baril<sup>52</sup> in their study of the decomposition of esters and acids. The methyl, ethyl, propyl, and butyl esters of monobasic aliphatic acids were not affected but esters of higher alcohols, i. e., amyl and above, decomposed over this catalyst into an unsaturated hydrocarbon and the monobasic acid. Aliphatic monobasic acids themselves were not affected. Esters of aromatic acids decomposed into an unsaturated hydrocarbon and the aromatic acid which, in turn, gave carbon dioxide and the aromatic hydrocarbon if the acid were monobasic. Cases were found where halogenated aliphatic acids decomposed, yielding carbon monoxide as one of the products.

Ebert<sup>13</sup> attempted to find a catalyst which would enable him to produce acetaldehyde from carbon monoxide and methane. A nickel catalyst proved to be the best to catalyze the decomposition of acetaldehyde into carbon monoxide and methane. Equilibrium was thought to have been reached in this decomposition but attempts to approach the equilibrium from the other side were not successful. A number of catalysts were tried out by Graeber and Cryder<sup>19</sup> in the dehydration of formic acid. At 280 to 360° a thorium-silica gel catalyst proved to be the most efficient as to yield and purity of carbon monoxide. The method offers a good way to prepare pure carbon monoxide from formic acid, in place of the liquid phase dehydration used at present. Singh and Krase<sup>45</sup> sought to develop a catalytic vapor phase synthesis of acetic acid from methanol and carbon monoxide under pressure. Active carbon impregnated with phosphoric acid was found to be an effective catalyst for this reaction but its life was limited. The influence of fuel and water gas conversion catalysts formed the basis of an investigation by Brewer and Reyerson<sup>5</sup> on the rate of production of hydrogen from lignite char at 600 to 800°. Catalysts were found which produced higher yields of water gas, with a corresponding increase in hydrogen as compared with untreated char.

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## Chapter VI.

### Inorganic Chemistry, 1933-1935.

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In his review for 1929-1932 H. I. Schlesinger rightly remarked that the field of pure inorganic chemistry has become considerably circumscribed in recent years. This is not because of lack of interest or of things to do, but rather because other subdivisions of chemistry have arisen which are concerned with specialized aspects of inorganic chemistry. Thus the original all-inclusive domain has become separated into a number of smaller kingdoms. In this case the subdivision is not regrettable, providing, of course, the broader aspects of chemistry are recalled with sufficient frequency.

From time to time it is pertinent to enquire whether all investigations carried out by chemists as scientists are worth while. We have no good criteria for a judgment. It might be said that when an investigation merely illustrates a principle which is well understood, then it is of doubtful value. To be sure, new results or new phenomena may be uncovered in routine investigations, and an effort should be made in the selection of the problems to make more probable these eventualities; however, one has sometimes the fear that such possibilities are remote. The distinction between data that have permanent value and are of practical importance, and results which merely add unnecessary confirmation to an accepted theory, should, of course, be made. There is the possibility too that a less pretentious result of the present may become important in the future; great wines do not come from handsome grapes. This possibility must not be overemphasized, however. It may well be considered the duty of the inorganic chemist to keep the more fundamental goals before the specialized groups, when we know what they are.

The present review must, of necessity, confine itself to inorganic chemistry as distinguished from physical chemistry, thermodynamics, molecular structure, and other specialized subdivisions. This leaves such topics as the discovery and description of new elements and new compounds as the field to be surveyed. It must be emphasized, however, that more often than not the most interesting and useful results arise in the course of studies in the specialized fields.

**New Elements.** The remarkable discovery of Curie and Joliot,\*

\* Curie, I., and Joliot, F., *Compt. rend.*, 198: 254 (1934).

Crane and Lauritsen,<sup>1</sup> and Fermi and his associates,<sup>†</sup> that it is now possible to bring about the transmutation of most of the known elements, has been of special interest to chemists. Of historical importance is the fact that that which the original chemists tried to attain is now possible. In most cases the transmutations have led to elements already known, but when uranium is bombarded with neutrons, at least one, and possibly three new elements result, namely, 93, 94, and 95. The first experiments by Fermi and his associates, showing the existence of the new elements, were not regarded as conclusive by some chemists. The subsequent experiments made by Grosse and Agruss<sup>2</sup> on the chemistry of 91 (protactinium) have clarified the doubtful points considerably and have led to experiments establishing the existence of the new elements. In this connection Grosse<sup>3</sup> has discussed the probable chemical properties of 93 and 94 from the point of view of the periodic law and Bohr's theory of atomic structure. In order to establish which element is formed in a transmutation process, purely chemical experiments are made in which the unknown element is mixed with another, assumed to be isotopic with it. This procedure was used by Livingston and McMillan<sup>4</sup> to show that nitrogen is changed to oxygen by deuteron bombardment, and by Yost, Ridenour and Shinohara<sup>5</sup> to establish that boron and carbon are converted into carbon and nitrogen, respectively, by deuteron bombardment. Further details on the physical side of transmutation will be found in the chapters on radioactivity and atomic structure.

The fact that the elements formed by neutron, proton, deuteron, and alpha particle bombardment are frequently radioactive may be employed to follow a given substance through various chemical reactions. Thus, Grosse and Agruss<sup>6</sup> have studied the exchange of bromine between bromide ion and bromine in solution of tribromide. They show also that the rate of evaporation of bromine from tribromide solutions at 100° is more rapid than the rate of bromine hydrolysis. It seems likely that the future will see further applications of the radio elements both in inorganic chemistry and in biology.

**The Noble Gases.** Chemists have made many attempts to cause the noble gases to combine with other elements. These efforts have, until recently, resulted in failures. The most important recent research in this field has been that of Booth and Willson,<sup>7</sup> who showed that argon and boron trifluoride, at low temperatures, combine to form the compounds, A.BF<sub>3</sub>, A.2 BF<sub>3</sub>, A.3 BF<sub>3</sub>, A.6 BF<sub>3</sub>, A.8 BF<sub>3</sub>, and A.16 BF<sub>3</sub>. In addition to this, the same authors<sup>8</sup> have made a study of the critical phenomena of A-BF<sub>3</sub> mixtures. An attempt to make xenon combine with chlorine and fluorine by

<sup>†</sup>Fermi, E., *et al.*, *Ric. scient.*, 2: 280 (1934).

sending an electrical discharge through mixtures of these gases was made by Yost and Kaye,<sup>9</sup> but no compounds were detected.

**The Halogens.** The most outstanding result obtained in this field is that of Cady<sup>10</sup> who prepared the compound  $\text{NO}_3\text{F}$  by the action of fluorine on dilute solutions of nitric acid. The substance is gaseous at room temperatures (b.p.  $-42^\circ$ ) and it explodes on heating. Yost and Beerbower<sup>11</sup> found that the same substance can be easily prepared by passing fluorine over solid potassium nitrate. They also found that at low temperatures and in the solid state  $\text{NO}_3\text{F}$  is dangerously explosive. It is disconcerting to note that foreign chemists have already designated it as a possible war gas. Cady<sup>12</sup> has investigated and clarified the reaction between fluorine and aqueous solutions of acids and alkalis and finds that little if any ozone is formed, but that  $\text{OF}_2$ ,  $\text{O}_2$  and peroxides are formed. The nature of the reaction products depends somewhat on the acidity or alkalinity of the solutions. By treating alkaline solutions with fluorine, Dennis and Rochow<sup>13</sup> found highly oxidizing substances which they suggested were salts of oxyacids of fluorine; Cady<sup>14</sup> considers that their results are due to the presence of oxyacidic salts of chlorine. Cady<sup>15</sup> has studied the system  $\text{KF-HF}$  and has given the most desirable mixtures to be used in electrolytic fluorine generators. A modified cell for preparing fluorine is described by Dennis and Rochow.<sup>16</sup> Ebert and Rodowskas<sup>17</sup> have prepared  $\text{AgF}_2$ , a powerful oxidizing agent. Eyring and Kassell<sup>18</sup> have shown that  $\text{H}_2$  and  $\text{F}_2$  do not react at room temperatures except in the presence of a catalyst, or when an initiating reaction takes place.

Ewart and Rodebush<sup>19</sup> have found that active nitrogen, formed in an electric discharge, reacts with  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$  to form the ammonium salts. A phase rule study of the system  $\text{PbI}_2\text{-KI}$  by van Klooster and Stearns<sup>20</sup> showed that  $\text{KPbI}_3$  exists. In the system  $\text{PbI}_2\text{-PbO}$  the compounds  $\text{PbI}_2\cdot\text{PbO}$ ,  $\text{PbI}_2\cdot 2\text{PbO}$ , and possibly  $\text{PbI}_2\cdot 4\text{PbO}$  are formed.<sup>20</sup> Willard and Thompson<sup>21</sup> have shown that under various conditions lead periodate precipitates have the formula  $\text{Pb}_3\text{H}_4(\text{IO}_4)_2$ . On heating this at  $275^\circ$ ,  $\text{Pb}_3(\text{IO}_5)_2$  results. Nichols and Willits<sup>22</sup> have made an extensive study of the compound formed when ammonia and Nessler's solution react and find it to be  $\text{NH}_2\text{Hg}_2\text{I}_3$ . It is very insoluble and the fine colloidal precipitate is negatively charged.  $\text{KPbI}_3\cdot 2\text{H}_2\text{O}$  is the only double salt found in the system<sup>23</sup>  $\text{KI-PbI}_2\text{-H}_2\text{O}$  at  $0^\circ$  and  $25^\circ$ . Ricci<sup>24</sup> has found that the double salts  $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 15\text{H}_2\text{O}$  and  $2\text{NaIO}_3\cdot 3\text{NaBr}\cdot 10\text{H}_2\text{O}$  are formed in the system  $\text{NaIO}_3\text{-NaBr-H}_2\text{O}$  at  $5^\circ$ ,  $25^\circ$ , and  $50^\circ$ . Cartledge and Goldheim<sup>25</sup> have made an extensive study of the complex ions and compounds formed in aqueous solutions of  $\text{HgCl}_2$  and  $\text{K}_2\text{C}_2\text{O}_4$ . They found that  $\text{HgCl}_2$ ,  $\text{HgCl}_2(\text{C}_2\text{O}_4)_2^{2-}$ ,  $\text{HgCl}_3^-$ ,  $\text{Hg}_2\text{Cl}_4$ , and  $\text{Hg}_2\text{Cl}_5^-$  were present in equilibrium in the solutions studied.

Dobbins and Colehour<sup>26</sup> have found that solutions of perrhenic acid,  $\text{HReO}_4$ , are best prepared by oxidizing Re or  $\text{ReO}_2$  with 30 percent  $\text{H}_2\text{O}_2$  and then evaporating the resulting solution until viscous.

**The Elements of the Sixth Group.** The many compounds of sulfur have been the subject of a large number of investigations in the past. With the introduction of improved methods of experimentation, a number of interesting investigations are now possible that formerly were too time-consuming or otherwise difficult. Shumb and Hamblet<sup>27</sup> have carried out a very thoroughgoing investigation of the reactions of  $\text{SOCl}_2$  and  $\text{S}_2\text{Cl}_2$  with lead oxalate and formate. They find that lead oxalate reacts quantitatively with  $\text{SOCl}_2$  to give  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{PbCl}_2$ . When  $\text{S}_2\text{Cl}_2$  reacts with lead oxalate, S,  $\text{SO}_2$ ,  $\text{CO}_2$ , and  $\text{CO}$  are the products. The reaction with lead formate is not simple. McCleary and Fernelius<sup>28</sup> have studied the oxidation reactions between oxygen and the alkali polysulfides, selenides, and tellurides in liquid ammonia solutions. Mixtures of the *ite* and *ate* salts are, in general, formed. It is gratifying to note that attention is being given to the interesting reactions that take place in liquid ammonia solutions. Barton and Yost<sup>29</sup> carried out vapor density and dissociation experiments on sulfur monochloride,  $\text{S}_2\text{Cl}_2$ , in the temperature range  $200^\circ$  to  $800^\circ$ , in order to determine the nature and extent of dissociation. Although the results were best explained by assuming  $\text{S}_2$  and  $\text{Cl}_2$  to be the dissociation products, the calculated heats of reaction were not in agreement with existing thermal data.

The anhydride of selenic acid has been prepared by Kramer and Meloche.<sup>30</sup> They caused selenium to react with oxygen in the negative region of a glow discharge. Anyone who has worked with telluric acid will be pleased to learn that it may be readily prepared by refluxing a mixture of tellurium dioxide, sulfuric acid, and 30 percent hydrogen peroxide. This method was found satisfactory by Gilbertson.<sup>31</sup> Claussen and Yost<sup>32</sup> found a new volatile fluoride of tellurium when they passed fluorine over tellurium. The exact formula was not determined, but it was established that each molecule contained two atoms of tellurium and had the possible formula  $\text{Te}_2\text{F}_6$ .

Oxygen compounds are, in general, best considered under other compounds. The existence and separation of the oxygen isotope,  $\text{O}^{18}$ , as a problem of interest in itself, has attracted considerable attention and rightly so, since more exact knowledge of nuclear and even molecular structure is to be obtained by working with the pure isotopes. Green<sup>33</sup> found some concentration of  $\text{O}^{18}$  resulted on the electrolysis of water. By extended electrolysis of an old commercial electrolyte, Hall and Johnston<sup>34</sup> established the separation factor to be 1.008, and found the concentration of  $\text{O}^{18}$  to be 4 p.p.m. (parts per million).

A modified and relatively safe method of preparing liquid ozone has been described by Byrns.<sup>35</sup> The ozone generator itself is operated at liquid air temperatures.

Further interesting and important results on the properties of the sulfur group elements have come from x-ray and electron diffraction studies. These results are to be looked for in the chapters dealing with these subjects.

The metals of the sixth group have not received a great amount of attention recently. Of interest is the study made by Windsor and Blanchard<sup>36</sup> of the properties of  $\text{Cr}(\text{CO})_6$ . They established the formula by vapor density measurements and, in addition, measured its vapor pressure as a function of the temperature. Ehret and Greenstone<sup>37</sup> have studied the decomposition products of  $\text{CrO}_4 \cdot 3\text{NH}_3$ ; at  $120^\circ$  the substance decomposes in a lively fashion to give  $\text{CrO}_3 \cdot \text{NH}_3$ , which is not a peroxy compound. Schlesinger and Hammond<sup>38</sup> have determined the formulas and dissociation pressures of a series of complex ammonia compounds of chromous chloride. The formulas of these complex salts are given by  $\text{CrCl}_2 \cdot n\text{NH}_3$ , where  $n$  has the values 6, 5, 3, and 2. Of considerable interest is the effect of chlorine on these substances. The ammonia groups are oxidized first, and the chromous chromium is not affected until all of the ammonia has been converted to nitrogen and hydrogen chloride. Fricke and Brownscombe<sup>39</sup> have found that the dichromates in sulfuric acid solution are reduced to chromic salts when irradiated with x-rays. The effect is due to the hydrogen peroxide formed by the action of the x-rays on the aqueous solution.

The magneto-optic method of chemical investigation has not yet been made sufficiently objective to be generally accepted as reliable. This writer has talked with people who have observed the effect and believe it to be real. He knows others who have tried and failed. If someone would only make it as nearly completely objective as possible, a number of purely chemical questions of importance could be settled with ease. Ball and Crane,<sup>40</sup> for example, have used the method to show that the dichromates are reduced, to a small extent, to pentavalent chromium. The method might find application in the study of chemical kinetics, in which intermediates are assumed to exist in small amounts.

Sears and Lohse<sup>41</sup> have shown that the products of the reaction between chlorine and intimate mixtures of tungstic acid and carbon are the volatile oxychlorides. The carbon is not consumed but acts as a catalyst only.

**The Elements of the Fifth Group.** The trinitrides have, since their discovery, been of great interest to inorganic chemists. This is perhaps due to the large number of reactions that they undergo and to the question of their structure. All will doubtless agree that Edward C. Franklin has been preeminent in this field. He has recently<sup>42</sup> discussed the nature of the trinitrides from the point of



view of their reactions, and concludes that they are salts of ammonio nitric acid. That is, the trinitrides are the ammonia system analogs of the nitrates. The reaction  $\text{KNO}_3 + 3 \text{KNH}_2 = \text{KN}_3 + 3 \text{KOH} + \text{NH}_3$  illustrates the general idea. Another American chemist who has made many worthy contributions in this field is A. W. Browne<sup>43, 44, 45</sup>. He and his associates have prepared and investigated the physical and chemical properties of ammonium trinitride, hydrazine trinitride, and azido dithiocarbonic acid. The last compound is an acid of about the same strength as sulfuric acid. It was also found that ammonium trinitride could be sublimed from mixtures of sodium trinitride and ammonium nitrate or sulfate.<sup>46</sup> Howard and Browne<sup>47, 48</sup> have discovered that when small tungsten filaments (0.05 mm.) are heated to 3000° under liquid ammonia, hydrazine is formed to the extent of some 0.25 percent. They determined the yield as a function of current consumption, temperature, and other factors. Nichols<sup>49</sup> determined the gaseous products resulting from the reaction between solutions of silver salts and hydroxylamine. An accurate determination of the normal density of ammonia was made by Dietrichson, Bircher, and O'Brien.<sup>50</sup> The results are not useful for an atomic weight determination due to uncertainties in the values of the gas law constants.

The action of antimony trifluoride, with antimony pentachloride as a catalyst, on phosphorus trichloride has yielded, in the hands of Booth and Bozorth,<sup>51</sup> the new gaseous compounds  $\text{PF}_2\text{Cl}$  and  $\text{PFCl}_2$ . They find that the same gases are formed when gaseous mixtures of phosphorus trichloride and trifluoride are heated to 200°. Pauling<sup>52</sup> has given a penetrating discussion of the proper formula for antimonious acid and concludes that  $\text{HSb}(\text{OH})_6$  best expresses the known properties. From the results of cell measurements, Carpenter<sup>53</sup> has concluded that pentavalent vanadium in acid solution is present as the ion  $\text{VO}_2^+$ . Coryell and Yost<sup>54</sup> had assumed the ion to be  $\text{V}(\text{OH})_4^+$  as a result of similar measurements. It is quite possible that Carpenter's conclusion is the correct one.

Grosse and Agruss<sup>55, 56</sup> have made an important advance in having prepared 0.1 gram of protactinium, element 91. They have determined some of its chemical properties and the nature of the compounds  $\text{Pa}_2\text{O}_5$  and  $\text{PaCl}_5$ . The chemical properties were made use of in clarifying the question of the existence of elements 93 and 94, as noted above under *New Elements*.

**The Elements of the Fourth Group.** The compounds of carbon come properly under organic chemistry, this classification being one purely of convenience. But because the reactions involved illustrate a type that is important at present in inorganic synthesis, the compounds obtained by Booth, Burchfield, Bixby, and McKelvey<sup>57</sup> are here noted. They treated  $\text{C}_2\text{F}_3\text{Cl}_3$ ,  $\text{C}_2\text{F}_2\text{Cl}_4$ , and  $\text{CFCl}_5$  with zinc in alcoholic solution and found that  $\text{C}_2\text{F}_3\text{Cl}$ ,  $\text{C}_2\text{F}_2\text{Cl}_2$ , and  $\text{C}_2\text{FCl}_3$ ,

respectively, were formed, two chlorine atoms being removed in each case. They attempted to convert  $C_2Cl_4$  to  $C_2F_4$  by treating the former with silver fluoride, but without success. Contrary to the statements encountered in some books, they found that carbon tetrachloride with silver fluoride does not give carbon tetrafluoride but a mixture of gases consisting principally of  $C_2Cl_2F_2$ .

More attention has been devoted recently to the compounds of silicon. Johnson and associates,<sup>58, 59</sup> applying a method used by Kraus, have shown that the silicon hydrides can be efficiently prepared by treating magnesium silicide with a liquid ammonia solution of ammonium bromide. They report yields of 70 to 80 percent. Booth and Stillwell<sup>60, 61</sup> have prepared and have determined the physical properties of the compounds  $SiHCl_3$  and  $SiHF_3$ . The first compound results from the reaction between silicon and hydrogen chloride, and the second compound is prepared from the first by treating it with antimony trifluoride and a catalyst, antimony pentachloride. Schumb and Bickford<sup>62</sup> have measured the boiling and freezing points of  $SiHBr_3$ . Booth and Swinehart<sup>63</sup> obtained the new compound,  $SiFCl_3$ , together with the corresponding substances containing two, three, and four atoms of fluorine, when they treated silicon tetrachloride with antimony trifluoride. Antimony pentachloride was used to catalyze the reactions.

An interesting study of the reaction between titanium tetrachloride and hydrogen at elevated temperatures was made by Schumb and Sundström.<sup>64</sup> Titanium trichloride is one product of the reaction and at about  $475^\circ$  this decomposes appreciably into the di- and tetrachlorides. Both the tri- and dichlorides were found to form ammonia complexes. The  $TiCl_2 \cdot 4NH_3$  decomposes at  $300^\circ$  to give a nitride of titanium. Roseman and Thornton<sup>65</sup> have developed a method for preparing iron-free titanous solutions.

Liquid ammonia as a solvent has found many applications in the field of organic synthesis and is being used more and more in inorganic preparations. Kraus and Carney<sup>66</sup> have applied it in the preparation of germanium hydride. They treated magnesium germanide with liquid ammonia solutions of ammonium bromide. The germanium hydride reacts quantitatively with sodium in liquid ammonia to give  $NaGeH_3$ . Dennis and Work<sup>67</sup> have found that monochlorogermane in liquid ammonia reacts to give germane and  $(GeH)_x$ , while dichlorogermane gives germanium. Germanium tetraiodide reacts with liquid ammonia with the formation of  $Ge(NH)_2$ .<sup>68</sup> Germanium nitride,  $Ge_3N_2$ , was obtained by Johnson and Ridgley<sup>69</sup> from the reaction between ammonia and germanium diiodide. The first product is an imide, and the nitride is formed by heating the imide at  $250-300^\circ$  for several hours. The recovery of germanium from germanite (a sulfide ore) has been very much simplified by the process discovered by Johnson, Foster, and Kraus.<sup>70</sup> The germanite is first heated at  $800^\circ$  in a stream of

nitrogen, and arsenous sulfide and sulfur are driven off. The residue is then treated with ammonia at  $825^{\circ}$ , which effects the reduction and volatilization of the germanium as  $\text{GeS}$ . About 99 percent of the germanium in the ore can be recovered. Dennis and Staneslow<sup>71</sup> have determined types of salts and their crystal forms that have  $\text{GeF}_6^-$  as the acidic constituent.

The effect of potassium on zirconium tetrabromide<sup>72</sup> in liquid ammonia and the action of some organic liquids on thorium tetrabromide<sup>73</sup> have been investigated.

**Elements of the Third Group. The Rare Earths.** The hydrides of boron have interested both experimental and theoretical chemists for some time. The kind of bond in diborane, especially, has given the theoretical people no end of trouble to explain. The results of the researches of Professor Schlesinger and his associates have been of importance in this field. Recently he has studied the reaction between diborane and boron trimethyl<sup>74</sup> and has found the compounds  $\text{B}_2\text{H}_5\text{CH}_3$  to  $\text{B}_2\text{H}_2(\text{CH}_3)_4$ . The reactions of these compounds with water indicate that to each boron is attached a hydrogen which is differently bonded than the others, an important result. Burg and Schlesinger<sup>75</sup> have also made a study of  $\text{B}_5\text{H}_{11}$  and its method of preparation. It results on allowing diborane to stand for long periods of time at room temperature, or, more effectively, by passing diborane through a tube heated to  $100\text{--}120^{\circ}$ . These authors<sup>76</sup> have prepared dimethoxyborine,  $(\text{CH}_3\text{O})_2\text{BH}$ , by means of the reaction between methyl alcohol and diborane. Burg<sup>91</sup> has prepared chlorodiborane by subjecting a mixture of hydrogen and boron trichloride to an electrical discharge. He also describes an improved method of fractional condensation. Sowa, Kroeger, and Nieuwland<sup>77</sup> have discovered a new hydroxyfluoboric acid to which they give the structural formula  $\text{H}(\text{HO}-\overset{\text{F}}{\underset{\text{F}}{\text{B}}}-\text{OH})$ . Schumb and Hartford<sup>78</sup> have prepared  $\text{BaSO}_4$ .

A careful determination of the physical properties and preparation of gallium trichloride and gallium was made by Craig and Drake.<sup>79</sup> Gallium melts at  $29.755^{\circ}$ , and the pure metal does not supercool. The extraction of gallium from germanite has been simplified by Foster, Johnson and Kraus.<sup>80</sup>

Indium trimethyl has been prepared and its properties determined by Dennis, Work, Rochow and Chamot.<sup>81</sup> They heated indium with mercury dimethyl at  $100^{\circ}$ . The indium trimethyl, a colorless solid, is rapidly oxidized by oxygen. Seward<sup>82</sup> prepared and measured the decomposition pressures of some hydrated normal and oxy sulfates of indium. Both indium and scandium were found in a zinc-free pegmatite ore by Romeyn.<sup>83</sup> Thallium triethyl was studied by Rochow and Dennis.<sup>84</sup>

The program of researches on the rare earths initiated by B. S. Hopkins has been continued. He and his co-workers have investigated the relative basicity of the rare earths and find that it increases with decrease in atomic number.<sup>85</sup> The rare earth oxides were found to react with dry ammonium chloride to give the anhydrous chlorides.<sup>86</sup> Of greater interest are the amalgams that Hopkins and his associates have prepared. By the electrolysis of concentrated alcoholic solutions of the chlorides with a mercury cathode,<sup>87</sup> and by the action of sodium amalgams on these solutions,<sup>88</sup> amalgams of the rare earth metals were obtained. In some cases it was possible to distill off the mercury and obtain the rare earth metals themselves. A novel method for the separation of europium from the other rare earths has been discovered by McCoy.<sup>89</sup> It consists in reducing  $\text{EuCl}_3$  solutions in a Jones reductor (zinc) to  $\text{EuCl}_2$  and allowing the reduced solution to run into a solution of magnesium sulfate. Europous sulfate precipitates out. An iodometric method of analysis for europium is also outlined. Yagoda<sup>90</sup> has pointed out the advantages of a conventional periodic classification of the rare earths for use in predicting their chemical properties.

**The Elements of the First and Eighth Groups.** Since the discovery of the hydrogen isotope, deuterium, by Urey in 1932, there have appeared a large number of articles dealing with this important substance. The majority of these papers deal with the physical properties of deuterium, such as the spectra of its compounds and its application in transmutation experiments. On the purely chemical side may be mentioned its occurrence, preparation, properties, and effects in reactions. Deuterium is present in all natural water. Gilfillan<sup>92</sup> reports, as a result of density measurements, that sea-water contains more deuterium than does tap-water. Using the electrolytic method discovered by Washburn, G. N. Lewis<sup>93</sup> prepared  $\text{D}_2\text{O}$  containing less than 0.01% H. Harkins and Doede<sup>94</sup> have also described an electrolytic method for separating  $\text{D}_2\text{O}$  from water. By electrolyzing  $\text{D}_2\text{O}$  (i. e., alkaline solutions in it), Selwood and associates<sup>95</sup> have concentrated a third isotope of hydrogen, tritium ( $\text{H}^3$ ). They report it to be present to the extent of 7 p.p.m. in water. Selwood and Frost<sup>96</sup> made determinations of the physical properties of  $\text{D}_2\text{O}$ , as did also Taylor and Selwood.<sup>97</sup> The latter authors give  $3.82^\circ$  as the freezing point of their highest density samples. Lewis<sup>98</sup> has observed a rapid interchange of H with D when  $\text{NH}_3$  is dissolved in  $\text{D}_2\text{O}$ .

The methods of x-ray crystal structure analysis were applied by Thomas and Wood<sup>99</sup> to the salts formed when mixtures of KF and NaCl are heated. They concluded that KCl and NaF were among the reaction products. Kraus and Parmenter<sup>100</sup> have examined the compounds formed when potassium in liquid ammonia combines with oxygen. They prepared  $\text{K}_2\text{O}_3$  and  $\text{K}_2\text{O}_4$

and established the existence of the hydrates  $K_2O_2 \cdot H_2O$ ,  $K_2O_2 \cdot 2H_2O$ , and  $K_2O_3 \cdot H_2O$ .

A very careful and complete investigation of the oxidation states of silver in nitric acid solutions was made by A. A. Noyes and his co-workers.<sup>101</sup> Saturated solutions of silver nitrate were oxidized with ozone and the dark colored solutions that resulted were analyzed and shown to contain bivalent silver. Measurements of electrode potentials and the rates of formation and decomposition gave added confirmation to the analytical results. It is necessary to assume the existence of trivalent silver in connection with the reaction mechanisms, and the black precipitate obtained on diluting the dark colored acid solutions probably consists of a trivalent oxide, but in solution the bulk of the silver is certainly bivalent. It is gratifying to have this question settled.

New ways for the preparation of nickel carbonyl have been developed by Windsor and Blanchard.<sup>102</sup> The method consists in shaking a suspension of nickel sulfide in an alkaline solution with carbon monoxide. The optimum yield is obtained from a suspension obtained from 1 f.w. (formula weight) NaOH, 0.1 f.w.  $Na_2S$ , and 0.5 f.w.  $NiSO_4$ , all in one liter. More interesting still is the substance  $CoNO(CO)_3$ <sup>103</sup> obtained by shaking an alkaline suspension of nickel cyanide with carbon monoxide and nitric oxide. In another communication Blanchard and Windsor<sup>104</sup> discuss the structures of the carbonyls. They conclude that, since  $Ni(CO)_4$  does not form compounds analogous to  $KCo(CO)_4$ , the cobalt carbonyl group has the nickel carbonyl electronic structure, the extra electron being furnished by the potassium.

The chemistry of the platinum metals has not received the attention it deserves. The one paper that contains matters of chemical interest in addition to physical chemical data is that of Kirschman and Crowell.<sup>105</sup> They studied the reaction between osmium tetroxide and hydrobromic acid at 100°. At low concentrations of  $OsO_4$  and acid and high concentrations of bromine, reduction to the septavalent form is indicated. A measurable equilibrium is attained. At higher acid concentrations tetravalent osmium is formed.

The system  $FeSO_4$ - $MnSO_4$ - $H_2O$  has been investigated by White.<sup>106</sup> Lange and Krueger<sup>107</sup> have prepared a copper ammonium sulfate dihydrate.

In two theoretical papers W. A. Noyes<sup>108</sup> gives consideration to the electronic structure of inorganic complexes, and the types of reactions from the point of view of current electronic theories.

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## Chapter VII.

# Analytical Chemistry, 1934 and 1935.

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**General Trends of Progress.** A review of the progress and advancements in research and development in analytical chemistry during 1934 and 1935 brings the conclusion that the period has been one of gratifying, and in some fields, unusual progress. Trends in progress have been towards unity of purpose and coordination of efforts. The contributions of new developments have met the demands of changes in the required method of attack to best suit the conditions. Such research has been prolific in leading to extended fields of application. Progress has been made possible by the analyst drawing upon many related scientific fields to reach the goal. Instrumental methods of analysis applied to all fields have made notable advances. The determination of small amounts of important elements in the presence of large amounts of foreign material is one of the problems particularly well met. The development of a new series of oxidation-reduction indicators with practical applications of note has been accomplished. The determination of small amounts of fluorine in water and of selenium in soils and plants or foods has demanded a concerted effort. The theory of the mechanism of the processes of precipitation has received an inspiring treatment and the complexity of the supposedly simple precipitation process has been clearly brought out. The application of the photronic process to studies in colorimetry and nephelometry have been numerous. New developments in the application of organic reagents as applied to colorimetry and to gravimetric precipitation processes are important. The study of comparative results in the determination of  $pH$  using indicator methods, the hydrogen, glass, and oxide electrodes, has resulted in the glass electrode gaining in preference for a number of reasons. Electrometric schemes of analysis have been well represented with conductimetric and electrodeposition methods not so prominent. American contributions following the development of the Heyrovský polarigraphic method of analysis were conspicuously absent. The complete scheme of analysis to be used in the quantitative separation and determination of the noble metals has



been described. Spectroscopic methods of analysis have offered contributions. The use of organic solvents has not been stressed to any considerable extent. Contributions in the field of alkali metal analyses have been quite unimportant. An interesting study is that of the catalytic reactions of silver as explained by the formation of argentic silver nitrate.

While it is not within the scope of this review to include the subject of physical testing of industrial materials, it is to be noted that during 1934 and 1935 published reports involving procedures of industrial physical testing have been numerous and of high quality. This, it would appear, indicates a beneficial influence being exerted by the prominence with which physico-chemical methods have, and are being, adapted to analytical chemical procedures. Mention of the important determination of electrode potentials has been omitted, notwithstanding its importance to instrumental methods of analysis, since it is strictly speaking physical chemistry in nature. Qualitative analysis, organic analysis, industrial gas analyses, microanalysis and atomic weight investigations are not included in this review. The attempt is made to emphasize the development only of the general trends in progress. The art of analytical chemistry is not in general to be recognized in the work of the accumulation of a large group of isolated processes. Rather the emphasis should be placed on schemes which are prolific and capable of systematized application to new developments, or which lead to a broadened insight of the theoretical backgrounds of known type reactions. It is by this emphasis that the trained research analyst may gain in prestige and the developments in the field will receive greatest impetus.

**Indicators.** A symposium on the subject of indicators is reported in *Chemical Reviews*. The historical aspects were presented by Brockman,<sup>1</sup> a system of indicators for use in determining the acidities of concentrated acid media was reviewed by Hammett<sup>2</sup> and the analytical applications of radioactive indicators was reviewed by Rosenblum.<sup>3</sup> The rather limited application of adsorption indicators was described by Kolthoff<sup>4</sup> with discussion of the mechanism of their action. The subject of the colorimetric determination of hydrogen ion concentration was taken up by Kilpatrick.<sup>5</sup> The study of the development of new indicators for oxidimetry was reviewed by Walden and Edmonds<sup>6</sup> and the greatly improved synthesis of the ideal oxidimetric indicator base *o*-phenanthroline was described by Smith and Getz.<sup>7</sup>

Probably the most valuable group of adsorption indicator studies, both the radioactive type of Paneth and the adsorption type of Fajans to which these types have been applied, was that of Kolthoff, Fisher and Rosenblum<sup>8</sup> and Kolthoff and Rosenblum.<sup>9</sup> Applying the radioactive indicator Thorium B, and the adsorption indicator wool violet (4 BN), to the very exhaustive study of the mechanism

of the processes involved in the precipitation of lead sulfate, has given rise to a most instructive series of conclusions. The results of this study indicate that the fresh precipitates of lead sulfate, though apparently well-formed microscopic particles, are in reality spongy masses of exceedingly minute amicroscopic crystals. The total surface of the precipitate is determined colorimetrically by measuring the adsorption of wool violet from dilute solutions of this dye in contact with the surface of the particles. The large size of its molecule prevents its adsorption by the sub-surface lead sulfate to which it is attached on the surface by expulsion of sulfate ions. The total surface exposed by the particles of lead sulfate is measured by the radioactivity of the isotopic Th B in both the precipitate and solution surrounding it. The surprising feature of this series of studies consists in the disclosure that the aging of precipitated lead sulfate results in the rapid diminution of external surface, produced, not by a rearrangement within the spongy mass of the particles themselves (the natural assumption originally made), but through the process of solution and reprecipitation. The investigation, as yet incomplete, has included a study of the ideal conditions for the precipitation of lead sulfate and the mechanism of the change in specific surface upon heat treatment of the freshly precipitated particles out of contact with the mother liquor. If the disclosures of this series of investigations can be safely applied by analogy to the case of other elements, for which we have no radioactive isotopes of sufficiently low half life, the mechanism of the general process of precipitation is disclosed in a most enlightening degree.

This type of study has been extended, including studies made possible through the use of artificial radioactive elements by Grosse and Agruss.<sup>10</sup> The extent of interchange of bromine in the inactive state with the bromine of activated sodium bromide was determined. The activation of sodium bromide was accomplished through bombardment by neutrons from the action of radon in contact with beryllium. The extent of the interchange of inactive for active bromine was measured by a Geiger-Müller counter, helium filled, and a thyratron operated watch. Except for the inability to use the electroscope in measuring activity, this method of attack holds great promise.

Although it is not correctly placed at this point, another study concerning the mechanism of crystal formation was that of Campbell and Cook.<sup>11</sup> The quite definitely established principle that microscopic crystals are more soluble than larger crystal magnitudes is doubted as shown by the study of strontium sulfate solubility equilibria. The effects are said to be those of super-saturation rather than augmented solubility. In this connection also, the correct composition of the precipitate obtained by the use of Nessler's reagent has been established by Nichols and Willits.<sup>12</sup>

The study of the mechanism of precipitation was further extended by the complete investigation of Walden and Cohen,<sup>13</sup> who made an x-ray study of the composition of precipitated barium sulfate. The contamination of the precipitate formed in the presence of nitrate ion was shown to result from solid solution formation rather than isomorphism, occlusion, or adsorption; long wavelength x-rays, using a calcium metal target, served in the determination of lattice parameters, with an accuracy of 0.01 percent.

New indicators for oxidimetry were studied by Hammett, Walden and Edmonds.<sup>14</sup> *o*-Phenanthroline and its nitro and amino derivatives were discussed. The indicator properties show them to be inferior to the plain indicator but prove that substitution in the organic molecule materially alters the potential of change of the ferrous complex. *p*-Nitro- and aminodiphenylamines as well as 2,4-diaminodiphenylamine were also prepared and studied. A study of the oxidation potentials of the phenanthroline-ferrous complex with variation in acidity was applied to the differential determination of iron and vanadium in ferro-vanadium, using ceric sulfate as oxidant. This study was made by the same authors.<sup>15</sup> They also studied the use of a silver reductor in the titration of iron in presence of vanadium<sup>16</sup>; this is valuable in the reduction of iron in the presence of titanium; molybdenum interferes. The method of Walden and coworkers<sup>15</sup> was further investigated by Willard and Young,<sup>17</sup> using  $\text{KMnO}_4$  in place of  $\text{Ce}(\text{SO}_4)_2$ . The use of lower acid concentrations are thus possible and the determination of Cr and V in steel is improved.

Diphenylbenzidinesulfonic acid has been prepared by Sarver and Fischer<sup>18</sup> and its use shows a smaller end point correction and tungsten does not interfere. A method for preparing diphenylbenzidine with 50 percent yields was described by Sarver and Johnson.<sup>19</sup> A system of hypobromite titrations using H. T. H. (low chloride) calcium hypochlorite was proposed by Kolthoff and Stenger<sup>20</sup> and its application to the determination of ammonia made, using a series of indicators previously described, of which Bordeaux was found best. A group of new indicators for dichromate titrations was described by Strada and Oesper<sup>21</sup> and benzoyl auramine G has been proposed as an indicator in Kjeldahl determinations by Scanlan and Reid.<sup>22</sup> Dichlorofluorescein as adsorption indicator was applied by Bambach and Rider.<sup>23</sup> A portable radium detector was described by Curtiss.<sup>24</sup>

**Colorimetry and Nephelometry.** Photronic colorimeters of various types were described by Wilcox,<sup>25</sup> Russell and Latham,<sup>26</sup> Müller,<sup>27</sup> Zinzadze<sup>28</sup> and Yoe and Crumpler.<sup>29</sup> A photronic turbidimeter was described by Bartholomew and Raby,<sup>30</sup> a photronic nephelometer by Greene<sup>31</sup> and by Furman and Low.<sup>32</sup> The simplicity of these instruments and the multiplicity of their applica-

tions indicate that colorimetric and nephelometric determinations in which they are used are becoming rapidly standardized.

A procedure for the preparation of uniform nephelometric suspensions, with description of the simple apparatus employed, was described by Scott and Hurley<sup>33</sup> and results given for silver chloride nephelometry. A thorough study of the preparation of permanent standards for use in the colorimetric determination of silica by the molybdate process was made by Swank and Mellon.<sup>34</sup> Potassium dichromate buffered with  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$  is recommended to the A.P.H.A. for recognition as an official method. A spectrophotometric study of ferric chloride in relation to the influence of free HCl and the conformity with Beer's law was reported by Mellon and Kasline.<sup>35</sup> The best range was found to be 0.02 to 0.5 molar in  $\text{FeCl}_3$  and 0.005 to 5 molar in HCl. The study was again made of the starch-iodine method for the colorimetric determination of iodine by Woodward.<sup>36</sup> Correction factors are given for the determination of 0.05-0.7 mg. of iodine per liter. The most important error is that due to dissociation of the starch-iodine compound. A statistical study of the uniformity of Lovibond red and yellow glasses was made by Walker<sup>37</sup> and by Gibson and Haupt.<sup>38</sup>

The most interesting contributions to the colorimetric research reports were those dealing with the determination of microquantities of lead in the presence of large amounts of vegetable and biological products. In these cases the various colorimetric modifications in the use of dithizone as color reagent have been employed. The titrimetric extraction method was used by Wilkins, Willoughby, Kraemer and Smith.<sup>39</sup> The sample (15 grams of blood or other biological materials) is decomposed, using a mixture of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ . A preliminary lead double extraction with technical dithizone in chloroform removes all the lead. The lead dithizone compound is oxidized to lead nitrate and the lead is then determined, using purified dithizone added in small portions until extraction is complete. Large amounts of iron do not interfere. Bi, Tl, and  $\text{Sn}^{++}$  interfere. An accuracy of 0.001 mg. Pb is attainable by this process. The process was extended by these authors<sup>40</sup> to include the separation of bismuth by dithizone at a pH of 2 followed by the regular<sup>39</sup> procedure for lead determination. A very complete study of the same determination was made in the case of spray residues by Winter, Robinson and Lamb.<sup>41</sup> Their method is also applicable to biological materials and includes lead determination in amounts from 0.005-0.04 mg. The semi-micro-determinations of lead was carried out by Randall and Sarquis.<sup>42</sup> They combined the method of electrodeposition as  $\text{PbO}_2$  with the colorimetric PbS determination of undeposited lead. Amounts between 2.5-15 mg. lead were determined with fair accuracy.

A novel new method for the determination of microquantities of

bromites was devised by Stenger and Kolthoff.<sup>43</sup> Hypochlorite was used to oxidize bromide to bromine which in turn oxidized phenol red to phenol blue. The bromide present was then determined colorimetrically. Chlorides do not interfere and iodides may be removed by use of nitrite. Manganese in sea water was determined by the only successful colorimetric method found by Thompson and Wilson,<sup>44</sup> namely, the periodate method. It has also been shown by Hough<sup>45</sup> that titanium interferes with the colorimetric persulfate oxidation to permanganate and the periodate method must be substituted. The colorimetric determination of molybdenum was described by Hurd and Reynolds<sup>46</sup> and by Stanfield.<sup>47</sup> The former use cyclohexanol in place of ether to extract Mo(CNS)<sub>3</sub>, while the latter use butyl acetate.

The determination of fluorine is represented by a group of papers. The work of Kolthoff and Stansby<sup>48</sup> uses the purpurin test in the range of 0.5-15 mg. and find the limit of detection at 0.005 mg. fluorine. The accuracy of their method is 2 percent and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{K}_2\text{Cr}_2\text{O}_7$  are used as color standards. Smith and Dutcher<sup>49</sup> use the quinalizarin reagent and advocate the use of  $\text{HClO}_4$  to distill out the fluorine in the presence of interfering elements. The same reagent was used by Sanchis<sup>50</sup> and a comparison of various methods was made by Smith.<sup>51</sup> The study of toxic quantities of fluorine leads to the determination that 0.9-1.0 p.p.m. and greater concentrations of lead cause mottled teeth. The microdetermination of fluorine in chloro-fluorides which are volatile has been made by Hubbard and Henne.<sup>52</sup> It is a combustion method, passing the volatile fluorine-chlorine compound over  $\text{SiO}_2$  at 900° C. and absorbing the products in NaOH. The fluorine is determined with cerous nitrate and the chlorine by the Volhard process; 1.10 mg. of fluorine can thus be determined.

The determination of selenium in biological materials was described by Dudley and Byers.<sup>53</sup> The method is colorimetric after reduction with bisulfite and accounts for 0.02-27 p.p.m. of selenium. A clinical procedure is given. The determination of selenium in soils, plants and tissues is described by Robinson, Dudley, Williams and Byers.<sup>54</sup> The colorimetric determination following HBr distillation is employed. The determination of selenium in the Colorado River waters was also described by Williams and Byers.<sup>55</sup> A colorimetric determination of silver used to sterilize swimming pool water is given by Schoonover.<sup>56</sup> This method uses the color reagent *p*-dimethylaminobenzalrhodamine and determines 1-40 p.p.m. There are a comparatively large number of interferences. The determination of copper in milk is described by Conn, Johnson, Trebler, and Karpenko,<sup>57</sup> using sodium diethyldithiocarbamate in basic solution after ashing and extraction of CuS from the ash. The spectrophotometric determination of ammonia after nesslerization is employed in the deter-

mination of amino-nitrogen in plant tissue as described by Pucher, Vickery, and Leavenworth.<sup>58</sup> The separation of amino-nitrogen is made after distillation in presence of MgO. Total nitrogen is determined on a separate sample and the amide nitrogen obtained by difference.

Numerous other colorimetric procedures have been described, which space does not permit considering individually.

**Electrometric Methods.** A device utilizing a radio tube circuit and amplification system to operate a buret cut-off for an automatically terminated oxidation-reduction titration has been described by Shenk and Fenwick.<sup>59</sup> A bimetallic (W-Pt) electrode system and arrangement to use only the power line voltage and one dry cell is applied. The titrations of ferrous iron with dichromate and the reverse titration, as well as the titration of zinc with ferrocyanide, are applied with results satisfactory to the ordinary degree of accuracy. The apparatus is said to be particularly serviceable in the case of large groups of routine analytical determinations.

The ferrous-ferric electrode potentials has been reinvestigated by Schumb and Sweetser<sup>60</sup> and by Bray and Hershey.<sup>61</sup> The values obtained were in fair accord but approximately 25 mv. higher than previous determinations. Many other studies of electrode potentials of direct interest in analysis have been investigated, which cannot be reviewed in a report of this length. One of the most interesting and valuable of such studies is that of Furman and Low,<sup>62</sup> namely, the use of the concentration cell in the determination of minute quantities of chloride in the presence of large amounts of ordinary reagents. The silver chloride electrode is used and to the unknown salt solution a known amount of chloride is added. The two cells, one, of the sample to which no chloride is added, and the other, with the chloride added, are connected. The junction potential is negligible and the correction for solubility of the electrodes was determined experimentally. The equation for the calculation is derived,  $E = 0.0591 \log [2(x + 0.01) / (x + \sqrt{x^2 + (4P_0/f^2)})]$ , where  $P_0$  is the solubility product of AgCl in water and  $f$  is the activity coefficient of AgCl when the solubility is  $P$ . The method is comparable in accuracy with the nephelometric procedure and foreign salts do not cause difficulty. Traces of chloride as small as  $3.5 \times 10^{-5}$  g. of chloride per liter were measured accurately. It would appear that this method can be extended in its application.

A direct reading pH meter for glass, quinhydrone and H<sub>2</sub> electrodes has been described by Hemingway,<sup>63</sup> which employs a ballistic galvanometer and voltage amplifier and having an accuracy of  $\pm 0.02$  pH units. A glass electrode potentiometer system was developed by Burton, Matheson and Acree<sup>64</sup> and a test of various determinations shows the glass electrode to agree with the isohydric indicator

method. Reliability tests of glass electrodes, including asymmetry tests,  $H_2$  electrode function and D.C. resistance, have been made by Laug.<sup>65</sup> A study of the choice of catalyst for the  $H_2$  electrode was made by Lorch.<sup>66</sup> Bright Pt or Ir deposits are recommended for low acidities and unbuffered solutions. Metallized glass quinhydrone electrodes are described by Newberry.<sup>67</sup> A modification of the Partridge vacuum tube potentiometer apparatus is described by Burton, Matheson and Acree.<sup>68</sup>

The application of the glass electrode to unbuffered solutions is discussed in a very complete paper by Ellis and Kiehl<sup>69</sup> and to dairy practice by Parks and Barnes.<sup>70</sup> The determination of the second ionization reaction of  $H_2CrO_4$ , using the glass electrode, was described by Neuss and Rieman.<sup>71</sup> A simple cell for glass electrode work as applied to the determination of the  $pH$  of leather extracts was described by Highberger and Thayer;<sup>72</sup> the glass electrode is the most satisfactory in determination of the  $pH$  of leather extracts as shown by Wallace,<sup>73, 74</sup> as also is the opinion of the committee on the determination of acid in leather;<sup>75</sup> it has been recommended to discontinue the Procter and Searle method.

The determination of the degree of olation in chrome tanned leathers using a conductimetric titration by Theis and Serfáß<sup>76</sup> was an important application of this type procedure; an electronic bridge balance indicator assembly for conductimetric titrations using a single amplification tube was described by Garman and Kinney.<sup>77</sup>

The electrodeposition of indium from a cyanide solution in the presence of *d*-glucose to give silver white deposits was described by Gray,<sup>78</sup> although the subject was not treated analytically.

The salt error and its influence upon quinhydrone electrode measurements was discussed by Hovorka and Dearing.<sup>79</sup> Several substitutes for the  $H_2$ , glass and quinhydrone electrodes have been described. A new type of antimony electrode, an oxide and sulfide electrode, was studied by Ball, Schmidt and Bergstresser.<sup>80</sup> No advantage over the ordinary antimony electrode was claimed. A benzaldehyde electrode as a substitute for the quinhydrone electrode in the  $pH$  range 7-13.64 was described by Herndon and Webb;<sup>81</sup> it has an accuracy of 0.2  $pH$  unit but is irreversible in nature. The germanium-germanium dioxide electrode was described by Nichols and Cooper<sup>82</sup> and not found to be constant and reproducible. The same authors<sup>83</sup> found some application for the electrode in spite of its non-reproducibility. A type of silver chloride electrode suitable for use in dilute solutions was described by Brown.<sup>84</sup> It gave results reproducible to  $\pm 0.02$  volts. A novel method for the preparation of silver-silver bromide electrodes was described by Keston;<sup>85</sup> both of these methods of preparing the electrodes should be of great value in the use of these electrodes in concentration cell work.

In the field of applied potentiometric determinations, some highly serviceable methods have been described. Willard and Young<sup>86</sup> describe the determination of small amounts of trivalent chromium in the presence of large amounts of chromic acid. The method uses  $\text{Ce}(\text{SO}_4)_2$  to oxidize chromium and nitrite to quantitatively titrate the excess. The method is accurate and the study of the influence of manganese has been made. The potentiometric determination of copper after precipitation as  $\text{CuCNS}$ , using the iodate oxidation in strong  $\text{HCl}$  solution process, was made by Hope and Ross.<sup>87</sup> Zinc and iron do not interfere. A mercury electrode potentiometric determination of thiocyanate was described by Kolthoff and Lingane.<sup>88</sup> An important contribution to the volumetric reduction process, using chromous sulfate, was described by Crowell and Baumbach<sup>89</sup> and was applied to the determination of osmium with very accurate results. The bismuthate method for manganese was studied by Park,<sup>90</sup> using arsenate and a W-Pt bimetallic electrode system. A potentiometric precipitation reaction was studied by Hanson, Sweetser and Feldman.<sup>91</sup> The arsenates are precipitated using  $\text{AgNO}_3$  in a 50 percent alcohol-water solution. The volumetric determination of iron in vegetable and chrome-tanned leather was described by Smith and Sullivan,<sup>92</sup> using titanous chloride and visual end point determination. Other potentiometric determinations have been applied, which space does not permit mentioning.

**Spectrographic Determinations.** The method of Nitchie was applied by Park and Lewis<sup>93</sup> for the determination of lead in copper. The copper is first precipitated from a 50 g. sample by co-precipitation with  $\text{CaCO}_3$  as  $\text{Pb}_3(\text{PO}_4)_2$ . The range covered was 0.0007-0.006 percent of lead. The spectrographic determination of lead in biological materials was studied by Cholak,<sup>94</sup> using the logarithmic sector procedure comparing lines of bismuth and of lead. The determination of bismuth, antimony, tin and molybdenum in copper was studied by Park,<sup>95</sup> using graphite electrodes and the Nitchie process. The elements were concentrated by co-precipitation with  $\text{MnO}_2$ , two precipitations being required. The spectral determination of fluorine in water, using graphite electrodes impregnated with calcium chloride, was carried out by Petrey.<sup>96</sup> The quantitative analysis of solutions by spectrographic study was made by Duffenbach, Wiley and Owens.<sup>97</sup> In this work the uncondensed spark between silver electrodes was applied to the determination of sodium, potassium, magnesium and calcium in samples of urine. The effect of one element upon the determination of the other was described. A spectrographic micro-determination of zinc is preliminarily described by Rogers,<sup>98</sup> using selenium as an internal standard. A spectrophotometric determination of copper as the ammonium complex was made by Mehlig.<sup>99</sup>

The application of ultraviolet spectrophotometry as applied to the



determination of the strength of very weak bases was studied by Flexser, Hammett and Dingwall.<sup>100</sup> A very complete paper on this new subject was presented. The logarithmic sector procedure with internal standards in the spectroscopic analysis of solutions was studied by Brode and Steed.<sup>101</sup> The pairs Co(Mn), Pb(Ni), W(Mn), Mo(Cr), Be(Bi), and Be(Mn) were studied. The range of determination is widest for cobalt, medium for lead, and small for chromium. The accuracy found was 12 percent down to 0.01-0.001 percent. The application of the spectrograph to the determination of carbon in steel was studied by Emery and Booth<sup>102</sup> and found unsatisfactory. The spectrophotometric determination of manganese in steel was studied by Mehlig<sup>103</sup> but no advantage was found over the bismuthate method.

**Separation and Determination of the Noble Metals.** A fascinating study of the separation and determination of the six platinum metals and their gravimetric determination was made by Gilchrist and Wickers<sup>104</sup> and represents a vast amount of research and its applications. The methods are also discussed by Gilchrist.<sup>105</sup> The separation of gold from tellurium is reported by Lenher, Smith and Knowles.<sup>106</sup> The gold is separated from the tellurium by preferential reduction using  $\text{NaNO}_2$  or  $\text{FeSO}_4$ , at a pH of 1. In this connection the unique and delicate process for the detection of certain rare metals by colored absorption on  $\text{Hg}_2\text{Cl}_2$  was reported by Pier-son.<sup>107</sup> The tests are extremely delicate and simple.

**Standards of Reference in Volumetric Analysis.** After many years of observance of the McBride method for the use of sodium oxalate as a volumetric reducing standard, particularly in the evaluation of  $\text{KMnO}_4$  solutions, this method has been found by Fowler and Bright<sup>108</sup> to give slightly low results. A new and corrective procedure is described. Potassium dichromate as a standard oxidimetric material was studied by Willard and Young,<sup>109</sup> using insufficient  $\text{K}_2\text{Cr}_2\text{O}_7$  to oxidize  $\text{As}_2\text{O}_3$ , with determination of excess  $\text{As}_2\text{O}_3$  using  $\text{Ce}(\text{SO}_4)_2$  in the presence of osmic acid and *o*-phenanthroline-ferrous complex as indicator. Foulk and Pappenhagen<sup>110</sup> have compared a simple method for the purification of silver with the atomic weight method of purification and have used this easily prepared silver as a standard in the evaluation of hydrochloric acid. Potassium ferro- and ferricyanides have been studied as reagents for standardizing titanous solutions by Smith and Getz.<sup>111</sup>  $\text{K}_3\text{Fe}(\text{CN})_6$  is particularly suited to the standardization of 0.01 *N* titanous solutions, because of the high equivalent weight. Potassium thiocyanate has been studied as a primary standard by Kolthoff and Lingane.<sup>112</sup> It is shown that it is suitable for ordinary accuracy in the Volhard procedure, which is accurate because of a compensation of errors. Potassium ferrocyanide is recommended as reference in case of  $\text{KMnO}_4$  for weak solutions by DeBeer and Hjort.<sup>113</sup> Preparation of pure  $\text{TiO}_2$  as

standard for volumetric comparison with titanous solutions was described by Plechner and Jarmus.<sup>114</sup> A new standard in acidimetry is furoic acid, studied by Kellog and Kellog<sup>115</sup> and an additional study of anhydrous sodium carbonate was made by Waldbauer, McCann and Tuleen.<sup>116</sup> They contend that sodium carbonate may be heated to 375-450° C. without dissociation, which is far beyond accepted values. Finally, a comparative study of drying properties of a large group of drying agents has been made by Bower,<sup>117</sup> which has proven of great value in properly classifying such materials.

**Miscellaneous Procedures.** A series of studies dealing with the role of silver salts in catalysis was reported by A. A. Noyes and collaborators. This topic is of great importance in analysis, since the oxidation potential involved is extremely high. The study of the preparation of argentic nitrate by the reaction of ozone upon nitric acid solutions of silver nitrate was described by Noyes, Hoard and Pitzer.<sup>118</sup> The presence of divalent silver as  $\text{Ag}(\text{NO}_3)_2$  and the comparative absence of the trivalent salt,  $\text{Ag}(\text{NO}_3)_3$ , was proven by Noyes, Pitzer, and Dunn,<sup>119</sup> while the oxidation potential of argentic nitrate in acid solution was shown to be approximately 1.94, which compares favorably with the highest of known values for other reactants as classified in this work. Nitric acid solutions of argentic nitrate are more stable than either perchloric or sulfuric acid solutions. The latter work was by Noyes and Kossiakoff.<sup>120</sup>

Fluorescence analysis was employed by Damon<sup>121</sup> for the determination of minute impurities of oxygen in gas mixtures. The usual blue ultraviolet fluorescence of acetone vapor is green in the presence of oxygen and the duration of the green color can be made the basis of a quantitative determination of oxygen. The technique, which is simple, is described and the results show that alkaline pyrogallol and yellow phosphorus for the absorption of oxygen are not nearly as sensitive. Oxygen can be determined in  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$  and  $(\text{C}_2\text{H}_5)_2\text{O}$ . The method would appear to have interesting possible extensions in analytical procedures.

The always troublesome separation of iron, aluminum and chromium from cobalt, nickel, zinc and manganese, for which process so many different methods of attack have been devised, is apparently better solved by the new method of Kolthoff, Stenger and Moskovitz.<sup>122</sup> Their precipitant is sodium benzoate and the separation is better than by use of the basic acetate method. Co-precipitation is reduced to the minimum while phosphate is not all removed. The precipitation of iron, aluminum, and chromium takes place in acetic acid solution.

A determination of small amounts of zinc in steel and iron was developed by Bright.<sup>123</sup> Three methods are compared. The separation of europium from other rare earths, depending upon its

reduction with zinc to the divalent form and precipitation under carbon dioxide as sulfate with magnesium sulfate, was described by McCoy.<sup>124</sup> The method serves for both purification and analysis. A separation of zinc from cobalt based upon a method using acrolein to prevent post-precipitation of cobalt was described by Caldwell and Moyer.<sup>125</sup> The use of 8-hydroxyquinoline in the separation of aluminum from beryllium and magnesium was reported by Knowles<sup>126</sup> and also in the separation of beryllium from aluminum, iron, titanium, and zirconium.

A modified persulfate-arsenite method for manganese in steel was described by Sandell, Kolthoff, and Lingane.<sup>127</sup> The oxidation of the manganese, using persulfate and silver, is followed by titration with arsenite containing nitrite to avoid the usual troublesome gray end point obtained in the absence of nitrite. Small amounts of chromium, vanadium, nickel, and molybdenum do not interfere. The Volhard chlorine determination has been cleverly modified by Caldwell and Moyer<sup>128</sup> in such a manner that, using a protective coating of nitrobenzene on the silver chloride precipitate, it need not be filtered before titration of excess  $\text{AgNO}_3$  by  $\text{KCNS}$ .

The vacuum induction furnace method for the determination of oxygen and nitrogen in steel was improved by Chipman and Fontana.<sup>129</sup> New features of the apparatus assembly are described and oxygen from alumina is included in the analysis. A rapid method for the determination of sulfur in ferro-magnetic alloys was described by Clarke, Wooten and Pottenger.<sup>130</sup> The method depends upon ignition in hydrogen with evolution of  $\text{H}_2\text{S}$ . The method is accurate to  $\pm 0.001$  percent.

The application of aeration to Kjeldahl nitrogen distillation is advocated by Meldrum, Melampy and Myers.<sup>131</sup> Fifteen minutes are required for the operation and inconveniences of boiling and bumping are eliminated, while the change in apparatus required is small.

The determination of tellurium in lead, which is recently in demand because of its increased use as an adulterant in lead cable sheath and tank linings as well as lead pipe, was worked out by Brown.<sup>132</sup> The method is undesirably long and will undoubtedly be much improved by additional work.

**Methods of Analysis Involving the Use of Perchloric Acid to Destroy Organic Matter.** A number of the developments previously mentioned have employed perchloric acid for various reasons. This reagent has rapidly become almost indispensable for use in the destruction of organic matter to be followed by determination of inorganic matter in the residue from large samples of various products. The digestion of biological materials prior to the determination of calcium and phosphorus was described by Gerritz<sup>133</sup> and, by the same author,<sup>134</sup> for the determination of phosphorus in urine. The destruction of organic matter in plant products using

perchloric and nitric acids to be followed by the determination of calcium, magnesium, potassium, and phosphorus was studied by Gieseking, Snider, and Getz.<sup>135</sup> The determination of iron in milk, blood, eggs, and feces, following the perchloric and sulfuric acid oxidation of organic matter after perchloric acid oxidation, was described by Leavell and Ellis.<sup>136</sup> Besides many other methods in which perchloric acid is employed, the greatly facilitated determination of chromium in leather was described by Smith and Sullivan.<sup>137</sup>

**Conclusions.** The necessarily restricted extension of available space for this summary of the progress of analytical chemistry in the United States in 1934-35 has caused a great number of worthy developments to go unmentioned which might well have been included. Many gas analytical procedures had to be omitted. Micro methods, in spite of their increasing number, were in general omitted. The attempt was made to classify and emphasize procedures having a unity of purpose. Those which lead to the solution of the more difficult of analytical problems as taught by past experience are most desirable of improvement. The review stamps at least one point as established, namely, that progress has been made in no uncertain degree and a standard of quality of a gratifying nature has been realized.

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## Chapter VIII.

# Applications of X-Rays in Metallurgy.

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X-ray techniques have a well-recognized position in metallurgy. In preparation for a formal symposium to be held in 1936, the American Society for Testing Materials conducted a preliminary survey of the field at a meeting in June, 1935, at which over forty short papers were presented; these, however, have not been published.

The purpose of this chapter is to review the applications of x-rays in metallurgy during the past year. Because of the wide range of interest, such a review cannot confine itself strictly to metallurgy. Mention will, therefore, be made of theoretical and related material which is of special interest in the metallurgical field. Articles dealing with structural data and electron diffraction phenomena are not included but it should be mentioned that the electron diffraction technique is rapidly becoming important in the study of corrosion of metal surfaces.

**General.** Two important books have appeared during this year. "X-rays in Theory and Experiment" by Compton and Allison,<sup>3</sup> while not dealing with the details of crystal structure analysis nor with the methods ordinarily applied in metallurgical problems, gives the fundamental background for the entire subject. Wyck-off's supplement to the second edition of his "Structure of Crystals"<sup>8</sup> gives a complete bibliography of x-ray structure work from 1930 to 1934 and critically reviews many of the newer structures.

Progress is being made by theoretical physicists in the understanding of the metallic state by applications of quantum and wave mechanics.<sup>7</sup> The temperature function of x-ray reflection in the neighborhood of the melting point of a crystal has been discussed briefly.<sup>5</sup>

Further advances have been made in the precise determination of lattice constants. An important contribution to this subject was made by Cohen,<sup>2</sup> who has devised a mathematical method of calculating lattice constants from powder diffraction data, so as to eliminate all errors, excepting those in the wave-length used in the computation. It applies particularly to symmetrical cameras

of the Debye, Sachs, or focusing types, and examples are given of applications to cubic, hexagonal, and orthorhombic structures. The particular advantage of this method is that it eliminates the systematic error, which in many cases far exceeds the accidental errors in measuring the diffraction angles. Jette and Foote<sup>6</sup> have given a detailed discussion of the inherent errors of symmetrical focussing cameras and their elimination by Cohen's method of computation. They emphasize that the precision attainable in lattice-constant measurements today has reached the point where the investigator must pay particular attention to the mode of preparation of materials for x-ray work. There are seldom deviations of as much as one part in ten thousand, between precision measurements of different investigators, using properly prepared materials of the same purity. Precise measurements of lattice constants for fourteen metallic elements are included in this article. Other applications of Cohen's method are given.<sup>15,17</sup> Short reviews of progress in diffraction methods<sup>4</sup> and the general application of x-rays<sup>1</sup> have been given.

**Equipment and Cameras.** A convenient and easily-constructed gas tube with interchangeable anti-cathodes is described by Walden and Cohen.<sup>17</sup> Buerger<sup>10</sup> gives designs of cathode assemblies for both Hadding and Shearer type gas tubes. Parratt<sup>16</sup> describes a method of evaporating metal films for use as x-ray targets. In this way targets of metallic elements, which are difficult to handle mechanically or to obtain by electrodeposition, for example, titanium, may be obtained. The use of alloy targets to obtain a larger number of diffraction lines within the limited range of angles covered by back-reflection focussing cameras, in order to increase the precision, has been described.<sup>6</sup> The targets used were binary alloys of approximately fifty atomic percent of each metal. An electric arc furnace has been used for casting molybdenum buttons in brass for use as targets in x-ray tubes.<sup>18</sup> Metallic calcium has been successfully used as a target.<sup>17</sup> A new needle valve for x-ray tubes<sup>13</sup> and the use of oil-diffusion pumps for gas tubes<sup>9</sup> have also been described.

For measuring the diffraction angles, a simple photometric device has been given<sup>6</sup> and the Geiger-Müller counter has been adapted for experiments where molybdenum K-radiation<sup>14</sup> is used.

Several modifications of back-reflection focussing cameras have been described, all of them providing for moving the specimen.<sup>6,17,15</sup> One of them<sup>6</sup> permits temperature control of the camera and the use of an inert gas atmosphere. Another<sup>17</sup> provides for either evacuation or filling of the camera with any desired gas. Norton<sup>15</sup> reviews a simplified technique for lattice parameter measurements with modified Sachs and focussing types of cameras. Goss<sup>12</sup> describes an equipment for studying metals at high tem-



peratures, while Frevel<sup>11</sup> gives a technique for x-ray studies of substances under high pressures.

**Solid Solution and Precipitation Hardening.** The determination of solubility limits by means of x-ray methods continues to be an important application of these methods. It may be remarked that the development of cameras and methods capable of high precision was required before such determinations could be carried out in a satisfactory manner. The methods which have proved most useful have been based upon large angle reflections in focussing cameras of either the Phragmén or symmetrical types and in the Sachs type. The extreme importance of proper annealing and quenching techniques of the sample actually exposed to the x-ray beam is now generally recognized.

Mooradian and Norton<sup>25</sup> have made an interesting study of the influence of lattice distortion on diffusion in metals. Their rather limited set of experiments showed that lattice distortion disappeared before diffusion began. The discussion of this subject by Mehl and Barrett immediately following the article should be mentioned.

DuMond and Youtz<sup>20</sup> attempted to make a grating for the determination of the absolute wave length of x-rays, by evaporating alternate layers of gold and copper on glass plates. They made the interesting observation that the diffraction maxima from such a grating decreased in intensity with time, which could be accounted for only by diffusion of copper and gold atoms into their neighboring layers. They suggest that this is a possible way of studying diffusion in the solid state.

Norton<sup>26</sup> has determined the solubility of copper in iron by x-ray methods and followed the changes in lattice parameters during aging. Jette and Fetz<sup>23</sup> determined the solubility of tin in nickel. Walters and Wells<sup>29</sup> used x-ray methods to assist in the determination of the solubility of iron in manganese. These methods were also used<sup>28</sup> in an attempt to determine the solubility of iron in zinc. This solubility was so small that results by this method were scarcely to be expected. Die casting alloys consisting mainly of zinc and aluminum are subject to certain slow dimensional changes after solidification. The nature of the change involved has been studied by Fuller and Wilcox.<sup>21, 22</sup> In the first article they showed that the decomposition of the beta-phase cannot be the sole cause for the shrinkage phenomenon. In the second paper it is proved that the shrinkage is due to the change in the composition of the alpha-phase, and that the extent of the shrinkage can be calculated from x-ray data.

Phillips and his co-workers<sup>19</sup> have continued their work on quenching stresses and also studied the precipitation reactions in Al-Mg and Cu-Al alloys. After confirming their earlier results on the existence of these stresses in quenched, massive material

(as compared to powders), they have calculated the stresses from lattice constant measurements by the method proposed by Barrett. They also studied precipitation rates by means of changes in lattice constants.

H. A. Smith<sup>27</sup> has studied isothermal diffusion reactions in austenite by several methods, including changes of lattice parameter with time, and the widths of the diffraction lines. He showed that the reaction curves determined by different methods generally do not agree. There has been considerable discussion as to whether the change in the lattice parameter would indicate the initial stages of precipitation from a solid solution. Opinions from various sources and mention of work as yet not published in detail have been given in E. J. Kennedy, Jr.'s column in *Mining and Metallurgy*.<sup>24</sup> The present opinion seems to be that microscopic examination is better for this purpose. This is quite reasonable, in the light of the nature of the phenomenon and the quantity to be measured, but Phillips, *et al*<sup>19</sup> find that when precipitation takes place in strained metal, when the atoms can diffuse more readily, the lattice constant changes throughout the entire solid-solution matrix.

**Constitutional Diagrams and Phase Identification.** Van Horn<sup>38</sup> has presented the x-ray evidence about the various constituents of steel. X-ray methods have been used in conjunction with the more classical methods of physical metallurgy in setting up the constitutional diagrams of the systems, Fe-Mn,<sup>29</sup> Mo-C,<sup>36</sup> Co-Mo,<sup>37</sup> In-Ag,<sup>30</sup> Fe-Cr,<sup>31</sup> and for the copper corner of the ternary systems Cu-Sn-Be.<sup>35</sup> McKeehan<sup>32</sup> has discussed the structure of MgZn and MgZn<sub>5</sub>. X-ray methods were also used to a minor extent in studying the polymorphism of the FeS-S solid solutions.<sup>33</sup> The oxide films formed during the wear of steels have been identified by x-ray methods as Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>.<sup>34</sup>

**Orientation of Crystals (Grains) in Metals, Preferred Orientation and Grain Distortion.** The determination of the orientation of a single crystal of a metal, when the crystal is thick, or imbedded in a mass of other crystals, has been a matter of considerable difficulty; this is now largely removed by Greninger's development of the back-reflection Laue method.<sup>44, 45</sup> He has applied this to the study of single crystals of copper.<sup>46</sup> Goetz and Dodd<sup>42</sup> have determined the direction of growth of bismuth and selenium crystals formed by condensation *in vacuo*. Mehl and Smith<sup>48</sup> have found that ferrite and pearlite assume a discreet number of determinate orientations which bear a direct relationship to the orientation of the original austenite. Barrett, Kaiser and Mehl<sup>39</sup> have reported work on the Widmanstätten figures in copper-silver alloys and find that previous theories for the mechanism of formation of such figures failed to explain their results. Post<sup>51</sup> has developed the experimental method of Davey and his co-workers for the determination of preferred orientations into a more rigid analytical procedure. It is applicable par-

ticularly to cubic metals. When applied to the earlier work of Davey on rolled silver, the analytical method yields somewhat different results. In the discussion of an article by Phillips and Dunkle,<sup>50</sup> Mehl reports the results of x-ray determinations on preferred orientations in some low-carbon steels. Goss<sup>43</sup> has studied preferred orientation in electrical strip steels of 3 to 3.5 percent silicon, in connection with the magnetic properties, using these studies to devise a method of preparing a strip steel of good magnetic properties. Bozorth<sup>40</sup> has studied some of the samples prepared by Goss but does not agree with the latter's determination of the orientation.

Mehl and Gensamer<sup>47</sup> show that the formation of Lüder's lines and of strain figures in annealed low-carbon steels is accompanied by a distortion which can be readily demonstrated by the peripheral widening of x-ray diffraction spots. Nusbaum and Goss<sup>49</sup> have studied grain distortion in metals during heat treatment by means of the radial asterism in Laue photograms. They find that the degree of cold work, the chemical composition, and the time and temperature of treatment are important in determining the presence or absence of "distorted" grain growth. Clark and Beckwith<sup>41</sup> give a method for detecting and evaluating residual distortion in crystals.

**Radiographic Inspection of Metals.** The use of x-rays for inspection of metals, particularly castings and welded sections, is increasing. More and more powerful tubes are being constructed which permit the application of these methods to materially greater thickness. Lippert,<sup>53</sup> for example, has reported in his column a new 400,000 volt installation which is used to inspect manganese steel sections five inches or more in thickness. There is also an increasing understanding of the necessity for proper x-ray technique and extensive correlation with other methods of examination to secure conclusive results.

Isenburger<sup>52</sup> has given a very useful set of x-ray exposure charts for steel. Moses<sup>54</sup> has given some results of using diffraction methods to study the existence of strains or preferred orientations in the immediate vicinity of fusion welds. A number of observations on castings and welds are reported,<sup>55-62</sup> which give a fair indication of the important position of this type of inspection in present-day industry. Occasional reports of this type may appear so widely scattered through engineering and other technical literature, that the bibliography of this section is probably not complete.

**Miscellaneous.** A number of articles on diverse subjects of possible interest to metallurgists have been reported. In a study of the solid phase reactions between certain carbonates and refractories, x-rays have been used to identify artificial mullite.<sup>67</sup> The diffraction of x-rays by liquid Na-K alloys in a magnetic field has been studied.<sup>65</sup> Waldo<sup>68</sup> gives a very complete tabulation of intensities and inter-planar spacings of 38 copper minerals for identification purposes. The conversion of quartz to cristoballite

in the presence of sodium silicate has been investigated.<sup>64</sup> Weiser and Milligan<sup>69</sup> report a new modification of ferric oxide monohydrate, which is of possible interest in connection with the rusting of iron. Clark, Lincoln and Sterrett<sup>63</sup> studied the orientation of polar molecules on metal surfaces with relation to wear and lubrication. Jesse<sup>68</sup> describes a simplified apparatus for quantitative chemical analysis by x-rays generated in a cathode-ray tube.

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## Chapter IX.

### Ferrous Metallurgy.

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In the past two years, there has been no diminution in the quantity or quality of research in ferrous metallurgy as reported in the transactions of the technical societies and in the metallurgical journals. In fact, both have increased; so many important papers have been published that it was difficult to choose those which represent best the recent progress. Moreover, it was necessary to omit reference to nearly all of the many papers—some of them very important from the practical viewpoint—which deal with the development of new steels for specific applications or the discovery of new uses for well-known materials.

**Pig Iron and Steel Manufacture.** Recent changes in the design and operation of the blast furnace have been of minor importance. Interest in beneficiation, not only of the ore but also of the blast, continues unabated. Oxygen enrichment of the blast, as a practical method of increasing thermal efficiency or speeding up chemical reactions, has not yet reached the experimental stage; so far, the progress in this field—if it can be called progress—has been confined to a discussion of whether or not blast beneficiation is economically feasible.

There have been a number of important contributions in the past two years to the physical chemistry of steel making. The fundamental work by the Metallurgical Advisory Board to the U. S. Bureau of Mines and Carnegie Institute of Technology, under the supervision of C. H. Herty, Jr., was closed with the publication, in book form, of Bulletins 64 to 69.<sup>1</sup> The first four of these report results concerning the effect of deoxidation on structure, age hardenability, and properties; Bulletin 68 is on iron oxide control in the basic open-hearth furnace; the last paper is a summary of knowledge of the various slag systems. The work by the Metallurgical Advisory Board over the past seven years has been of outstanding importance to the steel makers of this country; its influence should be felt for many years to come.

A symposium<sup>2</sup> on slag control was held late in 1934 by the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers. Papers were read on slag control in the

blast furnace (Sweetser), on the manufacture of rimming steel (Reinartz), low-carbon steel (Norris), high-carbon basic open-hearth steel (Reagan), rail steel (Washburn and Miller), alloy forging steel (Feild and Good), acid open-hearth steel (Foley), and basic electric steel (Walther). Kinzel concluded the symposium with a discussion of the physical testing of slag. The symposium attracted a large attendance and elicited an animated discussion.

The 1935 Howe Memorial Lecture to the Iron and Steel Division by E. C. Smith was also on slags<sup>3</sup> and included a broad survey of their constitution and the identification of the various constituents by petrographic methods. Other important papers on steel making were those by Arganbright<sup>4</sup> on the manufacture of basic open-hearth steel for cold-heading wire, Fleming<sup>5</sup> on the manufacture of rimming steels, Tranter<sup>6</sup> on ladle and teeming practice, and Nelson<sup>7</sup> on the effect of mold design on rate of solidification and soundness of ingots.

Dean, Barrett, and Pierson<sup>8</sup> summarized the properties of sponge iron—which has been attracting considerable attention lately—and showed that wrought iron made from this material has a cellular structure which is inherited from the sponge iron. An important contribution to the literature of steel making was the paper by Henning<sup>9</sup> on Bessemer steel, for which the author received the 1935 Robert W. Hunt Award by the American Institute of Mining and Metallurgical Engineers. The Bessemer process has received little or no attention metallurgically for many years. Chipman's paper<sup>10</sup> on the thermodynamics of deoxidation received the Howe medal as the most important contribution to the 15th annual meeting of the American Society for Metals. Chipman presented evidence to show that oxygen is present in liquid steel as dissolved oxide, probably FeO. Carbon exists in liquid iron and in austenite mainly as Fe<sub>3</sub>C. The deoxidizing power of the various deoxidizers was computed; in the order of increasing power at 1600° C. these are: Cr, Mn, Si, Ti, V, Zr, Al, Mg, and Ca.

**Inclusions and Gas.** As is characteristic of past years, most of the work on inclusions and gas has been on methods. Hoyt and Scheil<sup>11</sup> recommended the use of reflected polarized light in the study of inclusions, and Urban and Chipman<sup>12</sup> described the inclusions formed by deoxidizing liquid iron which had been previously saturated with oxygen. The inclusions were removed by a new technique and studied with the ore microscope. In a second paper,<sup>13</sup> these investigators identified and studied the constitution of inclusions in iron, melted in vacuum and in air, to which iron sulfide or titanium or zirconium had been added.

Progress to date at the National Bureau of Standards in the study of methods for the determination of oxygen was reported by Thompson.<sup>14</sup> Brower, Larsen, and Shenk<sup>15</sup> eliminated errors in the Ledebur method, so that they now believe that oxygen

values thus determined are definite and reproducible; but "the precise significance is still open to question, as indeed is true of all methods of oxygen determination so far developed." Hamilton,<sup>16</sup> on the contrary, in a paper on the determination of oxygen in alloy steels and its effect upon tube drawing, expressed the belief that oxygen may be determined by the vacuum-fusion method with an accuracy of 0.0005 percent, when proper precautions in sampling are taken.

Yensen and Herty<sup>17</sup> proposed a terminology and classification of non-metallic elements and gases in metal, which, it is hoped, will be the basis of an internationally adopted classification, or at least a starting point for discussions which will assist in eliminating some of the present confusion in nomenclature and classification.

In addition to the paper by Hamilton mentioned above, there are a few reports on the effect of inclusions on structure and properties. Reagan<sup>18</sup> determined the segregation of silicates in bottom-cast ingots, and Mahin and Lee<sup>19</sup> the influence of non-metallics upon the precipitation of primary cementite in hypereutectoid steel. In two important investigations, Yensen and Ziegler<sup>20, 21</sup> determined the effect of carbon and oxygen on magnetic properties of iron. The results were expressed in a ternary diagram. The latter paper<sup>21</sup> received the 16th Howe Medal award of the American Society for Metals.

**High-purity Iron and Iron-carbon Alloys.** The research of the world on the manufacture and properties of high-purity iron was correlated and critically reviewed in the sixth Alloys of Iron Research monograph, "The Metal—Iron".<sup>22</sup> Holmquist<sup>23</sup> determined the effects of stress on the transformation temperatures of iron, and Austin and Pierce,<sup>24</sup> by thermal expansion data on high-purity iron determined by a vacuum interferometer, were able to fix the  $A_3$  temperature at approximately  $910^\circ \text{C.}$ , which is in good agreement with the temperature chosen in "The Metal—Iron".<sup>22</sup>

There were a number of important papers on different phases of the iron-carbon system. Mehl and associates<sup>25</sup> reported further studies upon the Widmanstätten structure of high-purity iron and iron-rich alloys of iron with nitrogen and phosphorus. Schwartz<sup>26</sup> secured corroboration experimentally that in an iron-carbon alloy containing 0.03 percent silicon the reaction  $\text{Fe}_3\text{C} \rightleftharpoons 3\text{Fe} + \text{C}$  proceeds to the right at all temperatures from  $630^\circ \text{C.}$  to above the eutectic. Further light upon the important but still unsolved question of the stability of  $\text{Fe}_3\text{C}$  at low temperatures was supplied by Kinzel and Moore,<sup>27</sup> who found graphite in a 0.15 percent carbon steel which had been subjected to long heating somewhat below the eutectoid temperature; this indicates that cementite is unstable even below the  $A_1$  transformation. In an investigation of ferromagnetism, Zavarine<sup>28</sup> found that the recovery of magnetism during quenching does not take place at a single temperature but



over a temperature range. Other investigations which should be mentioned are those of Austin<sup>29</sup> on the dependence of the rate of transformation of austenite on temperature, and of Knight and Müller-Stock<sup>30</sup> on the transformation of austenite to martensite in which the martensite needles formed spontaneously.

There has been a marked re-awakening in interest in the structure of iron-carbon alloys, especially in the transitional structures which result from thermal treatment. One whole issue of "Metal Progress"<sup>31</sup> was devoted to a discussion of troostite and sorbite and to a consideration of the proper nomenclature for the structures now called by these terms but which are formed under different thermal treatments. Lucas<sup>32</sup> reported the results of a metallographic examination of nodular troostite, and Mehl and Smith<sup>33</sup> determined by x-ray methods the orientation of ferrite in pearlite with respect to the original austenite. In a paper on the application of thermomagnetic methods to metallographic research, Ellinger and Sanford<sup>34</sup> showed that martensite is relatively unstable but can be stabilized by reheating or by aging.

**Constitution of Binary and Complex Alloys of Iron.** Since the work of Smith and Palmer on copper steels in 1933 (This Survey, Vol. VIII: 213), the interest in copper as an alloy with iron has become widespread. The fourth Alloys of Iron Research monograph<sup>35</sup> was published in 1934 and gave a comprehensive critical summary of the constitution of iron-copper alloys and the effect of copper on the structure and properties of carbon steel, alloy steel, and cast iron. Norton<sup>36</sup> redetermined the solubility of copper in iron as 1.4 percent at 850° C. This decreases to 0.35 percent copper at 650° C. and is constant below this temperature. Norton also investigated lattice changes in aging.

The important research at Carnegie Institute of Technology on the constitution of iron-manganese and iron-manganese-carbon alloys, by Walters and his associates, which was mentioned in previous issues of the "Annual Survey" (Vol. VI: 200; Vol. VIII: 212) was completed with the publication of two papers.<sup>37</sup> One of the papers contained the iron-manganese diagram and the other the 7 percent manganese section of the ternary iron-manganese-carbon diagram.

Among the other papers on the constitution of iron alloys which should be mentioned are those of Ziegler,<sup>38</sup> who found that no appreciable diffusion resulting in a change of composition takes place in iron-silicon alloys during heat treatment, and of Schowalter, Delammater, and Schwartz,<sup>39</sup> who attempted to locate the metastable eutectoid point in Fe-C-Si alloys containing 1 percent silicon. An alloy with 100 percent pearlite has 0.92 percent carbon.

Chipman and Murphy<sup>40</sup> determined the solubility of nitrogen in iron as 0.04 percent at 1600° C. The temperature coefficient of solubility is small, about  $1.5 \times 10^{-5}$  percent per degree. Work on

iron-chromium alloys was reported by Hicks,<sup>41</sup> who studied the diffusion of chromium into iron, and by Austin and Pierce,<sup>42</sup> who determined the linear thermal expansion and studied transformation phenomena in low-carbon iron-chromium alloys containing 3 to 10.5 percent chromium.

**Properties of Carbon and Alloy Steels.** Normal-temperature properties of carbon steels were studied by Rosenberg and Jordan,<sup>43</sup> who investigated the influence of oxide films on wear, Phillips and Dunkle,<sup>44</sup> who determined directional properties of rolled and annealed low-carbon steels, especially ductility as shown by the cupping test, Polushkin,<sup>45</sup> who studied the effect of cold work on structure and properties of tubes drawn by three processes, Harvey,<sup>46</sup> who determined the effect of cold working on the properties of cold-headed bolts and who gave a heat treatment which would remove the effect of cold work in the head without materially affecting the properties of the cold-worked stem, and Cook,<sup>47</sup> who studied the relation between chemical composition and transverse fissures in rails.

Papers on the properties of low-alloy steels were numerous. Armstrong<sup>48</sup> gave a comparison of the mechanical properties of 25 low-alloy cast steels after 9 different heat treatments, and Critchett<sup>49</sup> summarized the mechanical properties and corrosion resistance of low-chromium steel castings containing up to 7 percent chromium.

As noted in a previous section, the properties of steels and cast irons containing copper have been reviewed and correlated in the monograph "The Alloys of Iron and Copper".<sup>35</sup> Epstein and Lorig<sup>50</sup> found that copper steels can be carburized successfully if the copper is 2.8 percent or below. A new copper alloy steel for sheet, containing 0.50 to 1.00 percent manganese, 0.50 to 1.50 percent copper, 0.50 to 0.80 percent nickel, 0.20 percent molybdenum, and 0.12 to 0.30 percent carbon, for which higher strengths are claimed, was announced by Miller.<sup>51</sup>

Phosphorus, long looked upon as a harmful impurity in steel, has been recently used as an alloying element. Progress in the development of the phosphorus-bearing steels was reported in a correlated abstract by Gillett.<sup>52</sup> A recent development in silicon steel for electric sheet was published by Goss,<sup>53</sup> who described the material as a fine-grained strip, the properties of which approach the properties of a single crystal.

The nitriding process is still of interest. Norton<sup>54</sup> presented data to indicate that the aluminum in nitrided steels is precipitated as aluminum nitride. This compound in finely dispersed form is the primary cause of the high hardness. Strauss and Mahin<sup>55</sup> reported the development of a new nitriding steel free from aluminum. The material contains about 2.5 percent chromium and small amounts of molybdenum and vanadium.

There were two important papers on fatigue, both from the

National Bureau of Standards. Shelton and Swanger<sup>56</sup> described a special long-span rotating-beam machine for determining fatigue properties of wire. The fatigue limits of cold-drawn wire with the original surface unmachined and unpolished were found to be 40, 60, and 82 percent of the fatigue limits of highly polished specimens of the same materials. McAdam and Clyne<sup>57</sup> reported the results of a large number of tests on ferrous and non-ferrous materials to show the effect of mechanically and chemically formed (corrosion-fatigue) notches.

Three papers on corrosion will be mentioned. Speller,<sup>58</sup> in the 1934 Howe Memorial Lecture to the Iron and Steel Division, American Institute of Mining and Metallurgical Engineers, gave a broad survey of the corrosion problem. Knight and Benner<sup>59</sup> compared the corrosion resistance of wrought iron, made by hand puddling, mechanical puddling, and the Aston process, in salt water, dilute acids, and air. Denison and Hobbs<sup>60</sup> made a report on the corrosion of steel in acid soils. This is a part of the comprehensive research on soil corrosion which has been going on for several years at the National Bureau of Standards.

**Effect of Temperature.** There were fewer investigations than usual on the properties of carbon and alloy steel at subnormal and elevated temperatures. Papers on properties at subnormal temperatures were given by Hiemke and Schulte,<sup>61</sup> who gave data on the impact resistance of 1.25 percent manganese plate steel at low temperatures, and by Campbell,<sup>62</sup> who found that the addition of nickel in small amounts tends to improve the low-temperature impact values. The amount of nickel depends on the carbon content and varies from 2 to 3.5 percent. Proper heat treatment is very important.

Another investigation of low-temperature properties was made by Heindlhofer,<sup>70</sup> who determined the relation between the abrupt change in impact strength at low temperatures and the plasticity of high-purity iron.

There were several important papers on creep. McVetty<sup>63</sup> gave an interpretation of creep tests; Wilson and Thomassen<sup>64</sup> found a secondary maximum in the creep strength of manganese-molybdenum steels at 480° C., which is paralleled by a precipitation-hardening effect detectable by x-ray examination; White and Clark<sup>65</sup> compared single-step long-time creep values with Hatfield's time-yield value and found that the latter is of importance as a qualitative test for classifying a series of steels of a given type at a given temperature but does not yield quantitative results in agreement with long-time creep values.

Cross and Johnson<sup>66</sup> determined creep properties of steel tubes containing 5 percent chromium and 0.5 percent molybdenum, and Sale<sup>67</sup> reported compression tests of structural steel at elevated temperatures. An investigation on the elevated-temperature

properties of 0.10 and 0.45 percent carbon steels with and without silicon, chromium, and molybdenum by White, Clark, and Wilson<sup>68</sup> indicated that these properties are dependent chiefly on the initial heat treatment and upon the alloying elements and may be independent of the carbon content. A report by Shelton<sup>69</sup> included thermal conductivity at elevated temperatures of ingot iron, wrought iron, cast iron, and carbon and alloy steels.

**Corrosion- and Heat-resistant Steels.** The unflagging interest in this class of materials is evidenced by the large number of reports of investigation and also by the appearance, in less than two years, of a second and enlarged edition of "The Book of Stainless Steels".<sup>71</sup> In addition to the use of titanium as an inhibitor of intergranular corrosion, Becket and Franks<sup>72</sup> recommended the use of columbium. When this element, to the extent of ten times the carbon percentage, was added to the 18 percent chromium 8 percent nickel (18-8) alloy, no intergranular embrittlement was noted below 650° C. Wells and Findley<sup>73</sup> investigated the corrosion resistance of 18-8 wire containing 0.15 to 0.20 percent carbon and discussed the advantages and disadvantages of this higher carbon content. The heat treatment of the wire at 815° C. for various lengths of time was investigated as a means of stabilizing this higher carbon material against intergranular corrosion, but it was found to be not so effective as the addition of titanium.

An investigation with wide implications reported by Franks<sup>74</sup> shows that it is practicable to add nitrogen to low-carbon high-chromium steels to limit the grain size and improve strength and ductility without unduly increasing brittleness. Other investigations of stainless steels include those reported by Sommer,<sup>75</sup> who studied the relation between plastic deformation in deep drawing and tensile properties, Grimshaw,<sup>76</sup> who recommended the addition of 4 to 6 percent manganese and 3 percent copper to retain the austenitic structure even after severe cold working, and Newell,<sup>77</sup> who correlated the structure, after the addition of a number of elements, with the ductility at elevated temperatures. An interesting study of oxide inclusions in stainless steel and ferrochromium, giving methods for differentiating between the two oxide phases present, was reported by Baeyertz.<sup>78</sup>

One of the recent outstanding improvements in heat-resisting alloys was revealed in a paper by Hoyt and Scheil,<sup>79</sup> who have developed an alloy containing 55 percent iron, 37.5 percent chromium, and 7.5 percent aluminum for use in resistor electric furnaces. The alloy has many times the life of the standard nickel-chromium resistance alloys; moreover it can be used at higher temperatures, up to 1300° C. or even above.

Scaling tests were made by Kosting,<sup>80</sup> who determined the deterioration of chromium-tungsten steel in ammonia gases, and by Rickett and Wood,<sup>81</sup> who studied the action of oxygen and

hydrogen sulfide on iron-chromium alloys containing up to 28 percent chromium. The effect of alloy composition and kind of atmosphere was determined; it was found that hydrogen sulfide causes much more pronounced scaling than oxygen.

**Heat Treatment and Aging.** A few of the papers already mentioned under "high-purity iron and iron-carbon alloys" might with justification be also mentioned under heat treatment and aging; especially the reports of Zavarine,<sup>28</sup> Austin,<sup>29</sup> Knight and Müller-Stock,<sup>30</sup> and Ellinger and Sanford.<sup>34</sup>

Reports which also deal with constitutional changes but which are more important as discussions of the theory of heat treatment are those by Nielsen and Dowdell<sup>82</sup> on the relation of stress to the transformation of austenite to martensite, and by Upton<sup>83</sup> on the habits and laws of decomposition of supercooled solutions with special reference to austenite.

Scott, who for some time has been investigating quenching rates, presented two papers. In the first,<sup>84</sup> he studied the application of the laws of heat conductivity to the cooling rate of steel cylinders in quenching. The thermal constants for certain steels and for important quenching media were evaluated. In the second paper,<sup>85</sup> Scott showed that there were three stages of heat transfer in quenching; of which the manifestations are: (a) a vapor blanket which momentarily retards cooling, (b) the carrying away of the heat by the vapor, and (c) cooling by convection. Other papers on heat treatment were those of Hughes and Dowdell<sup>86</sup> on the effect of quenching steel in hot lead on the mechanical properties, and a comparison of the properties of steel treated in this way with the properties of similar steels after quenching and tempering, and of Nusbaum and Goss<sup>87</sup> on grain distortion in metals during heat treatment as determined by the x-ray. McMullan<sup>88</sup> reported the properties of the case and core of a large number of carburized and heat-treated carbon and alloy steels, which showed the effect of grain size. Two papers on furnaces should be mentioned. Mawhinney<sup>89</sup> discussed heat transfer in fuel-fired furnaces, and Weinland<sup>90</sup> presented a graphical method of calculating heat loss through furnace walls.

Heat treating in controlled atmospheres, which has lately become of outstanding commercial importance in the annealing of sheet, received much attention. One of the most important of the several papers is the correlated abstract and critical summary of advances in this field which was published serially in "Metals and Alloys,"<sup>91</sup> Results of annealing in mixed gas atmospheres were reported by Marshall<sup>92</sup> and of gaseous carburizing by Austin,<sup>93</sup> who showed to what extent decarburizing and recarburizing might take place if the composition of the furnace atmosphere changed. Data on the amount of scaling in a low-carbon steel at 900 to 1150° C., depending upon the furnace atmosphere, were presented by Siebert and Upthegrove.<sup>94</sup>

The subject of age hardening, as was to be expected, was covered by a large number of papers. The present status of this phenomenon and its theoretical aspects were discussed by Harrington.<sup>95</sup> Ellinger and Sanford<sup>96</sup> investigated the constitutional changes taking place in an 0.80 percent carbon steel aged at room temperature and 100° C., using thermomagnetic analysis (cf.<sup>34</sup>), and Kenyon and Burns<sup>97</sup> presented methods for testing low-carbon sheets for blue brittleness and for stability against changes in aging.

Two conflicting views on the rôle of oxygen in aging were presented. Burns<sup>98</sup> claims that carbon is the cause of aging in nitrogen-free steels and nitrogen is responsible in nitrogen-bearing steels; oxygen apparently plays no significant part in either. Davenport and Bain<sup>99</sup> recognize two types of aging, one of which is caused by carbon, while the other, called strain aging, is caused by an iron-oxygen compound in the slip bands of cold-worked grains, which was rejected from material supersaturated with oxygen. Sauveur<sup>100</sup> studied the aging of cold-worked or quenched carbon steels in the light of the precipitation theory. Nitrogen and oxygen greatly increase the tendency of the material to age. The amount of aging depends upon the amount of free ferrite. To reduce or eliminate aging, Sauveur suggests that the material be quenched to form martensite and that the martensite be tempered to the hardness desired.

Aging in 4 to 6 percent chromium steel was investigated by Wilten and Dixon,<sup>101</sup> who found that the brittleness after long exposure at 480° C. is similar to that resulting from duralumin-type aging. In the 9th Campbell Memorial Lecture to the American Society for Metals, Krivobok<sup>102</sup> gave data on the effect of temperature on iron-chromium and iron-chromium-carbon alloys. The hardening of these materials after aging is caused by nitrogen.

**Grain Size.** One of the outstanding technical meetings of the past two years was the symposium on grain size held late in 1933 by the American Society for Metals and published in the 1934 *Transactions*. Twelve papers were presented. The symposium was arranged so that the papers would, so far as possible, cover broadly the field of ferrous metallurgy.

The control of grain size in the manufacture of basic open-hearth steel was discussed by Epstein, Nead, and Washburn,<sup>103</sup> and the relation between the grain size and the machinability and other properties of Bessemer screw stock by Graham.<sup>104</sup> Papers giving data on the relation between grain size and the following properties were presented: hardness and toughness of automobile steels,<sup>105</sup> structure and properties of medium-carbon (1040) steel,<sup>106</sup> forging properties and machinability,<sup>107</sup> tensile strength, impact resistance and creep strength at high temperatures,<sup>108</sup> sheet for deep drawing,<sup>109</sup> impact properties,<sup>110</sup> and magnetic properties of 5 percent silicon steel.<sup>111</sup> The P-F (penetration-fracture test) characteristic

of steel was discussed by Shepherd.<sup>112</sup> This test affords a simple and rapid means of distinguishing between high-carbon steels of the same chemical composition. The penetration in units of  $\frac{1}{64}$  inch of hardening by quenching under standard conditions plus the grain size number from a fracture test gives a numerical value which can be used to grade the steel.

The relation between grain size of the austenite and the prior heat treatment was discussed by Grossmann<sup>113</sup> and the relation between grain size and hardenability and normality of steels by Davenport and Bain,<sup>114</sup> also at the symposium. Other papers on grain size which should be mentioned are those of Herty<sup>115</sup> on the effect of deoxidation on grain size, hardenability, aging, and impact resistance at low temperature, and of Sefing and Trigger<sup>116</sup> on the relation between grain size and cracking or distortion in quenching medium-carbon steels. In the 10th Campbell Memorial Lecture to the American Society for Metals, McQuaid<sup>117</sup> summarized progress to date in controlling grain size in commercial steels, and the relation between the aluminum addition to the molten metal and the resulting grain size, hardenability, and pearlite divorce.

**Tool Steels.** A report by Digges and Jordan,<sup>118</sup> which might have been classified under grain size, contained data on the effect of the original structure of carbon tool steel on the austenite grain size and the critical cooling rate and hardening temperature. Properties of tool steel were investigated by Luerssen and Greene,<sup>119, 120</sup> who developed a torsion impact test which showed peaks of maximum toughness with low tempering temperatures. The location of these peaks could be varied by varying the heat treatment.

Three papers on high-speed steel will be mentioned. Garratt<sup>121</sup> described a new steel containing about 1.5 to 2.0 percent tungsten, 8 percent molybdenum, about 3.75 percent chromium, and 1 percent vanadium. This is apparently the newest development in molybdenum high-speed steel, a class of material which has been attracting considerable attention lately. Phillips and Weldon<sup>122</sup> investigated the effect of furnace atmosphere on the grain size of molybdenum high-speed steel. Liedholm<sup>123</sup> reported a study of retained austenite and its decomposition in cobalt high-speed steel. One paper was published<sup>124</sup> on the manufacture, heat treatment, properties, and uses of 2 percent carbon 12 percent chromium tool steel with and without vanadium or vanadium and molybdenum.

**Cast Steel and Cast Iron.** In a symposium<sup>125</sup> on the porosity of steel castings Sims gave data on proper mold and pouring practice to reduce porosity, Batty discussed molds and cores, and Woodward the mechanism of porosity.

Of the large number of papers on cast iron only a few, most of which are on alloy iron, will be mentioned. Saeger and Ash<sup>126</sup>

reported the results of the research going on at the National Bureau of Standards on the properties of gray iron as affected by casting practice, and Morken<sup>127</sup> and Eddy<sup>128</sup> gave data on heat treatments which result in improved strength, ductility, and resistance to shock and fatigue. Toüceda<sup>129</sup> described a fluidity test for cast iron, and Dahle<sup>130</sup> gave data on the impact resistance of plain and molybdenum cast irons at elevated temperatures. In a study of unalloyed malleable iron, Sauveur and Anthony<sup>131</sup> found that by varying the annealing practice malleable iron could be produced which had a ferritic, pearlitic, or sorbitic matrix.

As may be judged from the number of papers published recently, the use of copper as an alloy in cast iron is increasing. Eddy<sup>132</sup> reviewed the effect of copper on the structure and properties. Smith and Palmer<sup>133</sup> found that copper accelerates graphitization, reducing the annealing time about 50 percent. Moreover, copper induces precipitation hardening. Lorig and Smith<sup>134</sup> found that as much as 3 percent copper is soluble in white iron, and that from 0.70 to 1.50 percent improves the fatigue strength of the resulting malleable. Less than 0.50 percent has no effect. Precipitation hardening may be induced if the copper exceeds 0.70 percent.

Other reports on alloy cast iron are those of Vanick,<sup>135</sup> who gave properties and uses of cast iron to which nickel, copper, and molybdenum had been added, of Wood,<sup>136</sup> who reported thermal expansion characteristics of some nickel cast irons, including specimens containing nickel and copper in the monel ratio (70-30), and of Pennington and Jennings,<sup>137</sup> who studied the effect of tungsten and manganese on the graphitizing rate of white cast iron. Both of these elements promote carbide stability; the time for graphitizing reaches a maximum with 3 percent manganese; the effect of tungsten depends upon the manganese content.

Phillips<sup>138</sup> gave data on the heat and corrosion resistance of irons containing 20 to 35 percent chromium. The castings were made with ferrochromium containing nitrogen to control the grain size. Phillips also described the melting practice and structure and gave typical mechanical properties. The use of zirconium as a deoxidizing agent and as a graphitizing accelerator was recommended by Hall.<sup>139</sup> Nitrided cast iron has recently come into use for automotive parts, such as cylinder liners, cams, and the like, which should have high resistance to wear. The base iron usually contains chromium, aluminum, molybdenum, and occasionally vanadium. The properties and structure of this material have been described by Colwell<sup>140</sup> and by Homerberg and Edlund.<sup>141</sup>

**Miscellaneous.** A recent Alloys of Iron Research monograph<sup>142</sup> was prepared to explain the fundamentals of thermodynamics and the construction of binary, ternary, and higher phase diagrams to chemists, metallurgists, and others to whom the original work of



Gibbs and some of the diagrams now appearing in the regular Alloys of Iron Research monographs and other publications are incomprehensible.

Two papers on non-destructive inspection should be mentioned. Isenburger<sup>143</sup> published x-ray exposure charts for steel, and Norton and Ziegler<sup>144</sup> investigated the sensitivity of gamma-ray radiography. They found the sensitivity nearly constant for sections of 2.5 to 6 inches of iron or steel.

In a very interesting and provocative paper, entitled "A Chemical Engineer Views the Steel Industry," Ramseyer<sup>145</sup> gave the metallurgists and steel makers of this country his opinion of the inefficiency of their industry. While much of Ramseyer's trenchant criticism is undoubtedly justified, the very high cost of large-scale research at steel-making temperatures makes the investigation of most of his suggestions a matter for the distant future. Whether we agree with him about our inefficiency and the need for such drastic changes in practice, the viewpoint expressed was refreshing.

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# Chapter X.

## The Platinum Metals.\*

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Since the chapters prepared by Wichers<sup>1, 2</sup> in Volumes II and III of the Annual Survey of American Chemistry, in which the subject matter was restricted to the inorganic and analytical chemistry of silver, gold, and the platinum metals, no account of the platinum metals has appeared in this series of reviews. In the present chapter, only the platinum metals are considered, and the attempt has been made to include all of the published work of American origin during the three-year period 1933-1931.

**Economics.** The annual chapter<sup>3, 4</sup> on platinum and allied metals, prepared by Davis for the Minerals Yearbook of the Bureau of Mines, contains statistics on the production, purchase, market, and price of domestic crude platinum; on the price and consumption of refined platinum metals; on the stocks of platinum metals in the hands of refiners in the United States and on the amounts sold by them to consuming industries; on the imports of platinum metals into the United States and the exports therefrom; as well as on production in foreign countries and on world production. Roush,<sup>5, 6</sup> during the same period, covered much the same sort of statistics.

The average yearly price of platinum remained practically stationary during 1932 and 1933, at \$32.00 and \$30.75 a troy ounce, respectively. Improved activity in the industries using platinum and restriction on the use of gold for industrial purposes are reflected in the sales of platinum metals by refiners in the United States in 1933, which amounted to 107,821 ounces, an increase of 29 percent over 1932.

**Chemistry.** *Analytical and Inorganic.* With the publication of two papers by Gilchrist<sup>7, 8</sup> and of two by Gilchrist and Wichers,<sup>9, 10</sup> the development of an analytical procedure by which the six platinum metals can be separated from one another quantitatively, in the absence of other elements, and determined gravimetrically, has been completed. The order in which the separations are made is:

\* Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

osmium, ruthenium, platinum, palladium, rhodium, iridium. In turn osmium, and ruthenium are isolated by distilling their respective tetroxides. Palladium, rhodium, and iridium are separated jointly from platinum by precipitating them hydrolytically as hydrated dioxides. Palladium is separated from rhodium and iridium by precipitating it with dimethylglyoxime. Rhodium is separated from iridium by reducing it to metal with titanous chloride. Titanium, introduced as reagent, is separated from iridium by precipitating it with cupferron.

The distinctive features of the method, by which it differs from traditional methods, consist in the conditions under which ruthenium is separated; the reagent solution used to absorb the liberated tetroxides of osmium and ruthenium; the application of controlled hydrolytic precipitation to the separation of platinum from palladium, rhodium, and iridium, either singly or jointly; the recovery of osmium, of ruthenium, and of iridium by hydrolytic precipitation; the separation of rhodium from iridium by titanous chloride; and in the avoidance of the use of potassium chloride, ammonium chloride, pyrosulfate fusions, and of extraction of metallic mixtures with acids.

A valuable contribution to the analytical chemistry of the platinum metals was made by Whitmore and Schneider,<sup>11</sup> who studied, with the aid of the microscope, the reactions of the six platinum metals (and also gold) with 33 different reagents, and developed for them a scheme of microscopical qualitative analysis.

Ogburn and Brastow<sup>12</sup> published a method for the separation of palladium from the other platinum metals by reduction with ethylene. They reported the error in the determination to be 0.75 percent. Hopkins<sup>13</sup> outlined a procedure for the assay of black sands, while Byers<sup>14, 15</sup> studied the effect produced by the metals of the platinum group on the surface of beads obtained by cupellation. Pierson<sup>16</sup> described tests for the estimation of small amounts of palladium and platinum, which involve reduction to metal by mercurous chloride and comparison with known quantities reduced in a similar manner. Haigh and Hall<sup>17</sup> described a procedure for the recovery of platinum used in potash determinations, which consists in precipitation of the platinum by zinc.

A new value for the atomic weight of osmium, 191.5, based upon the determination of the average osmium content of ammonium chloroosmate,  $(\text{NH}_4)_2\text{OsCl}_6$ , and of ammonium bromoosmate,  $(\text{NH}_4)_2\text{OsBr}_6$ , by Gilchrist,<sup>18</sup> was adopted by the Committee on Atomic Weights<sup>19</sup> of the International Union of Chemistry in 1934. This is the first change in the atomic weight of osmium since the value 190.9 was determined by Seubert<sup>20, 21</sup> in 1891, only one investigation having been undertaken in the interim, namely that of Seybold.<sup>22</sup>

Kirschman and Crowell<sup>23</sup> studied the reaction between osmium tetroxide and hydrobromic acid in a closed tube at 100° C. More recently, Crowell and Baumbach<sup>24</sup> described a method for the potentiometric determination of osmium in potassium chloro- and bromosmate, using chromous sulfate, with a reported error of less than 0.2 percent. Brunot,<sup>25</sup> from a medical point of view, investigated the toxic effect of osmium tetroxide on white rabbits. The animals showed evidence of acute irritation shortly after exposure began, soon became semi-comatose, and died somewhat later. The lungs were found to be particularly affected and death was attributed to purulent broncho-pneumonia.

Wichers<sup>26, 27</sup> described the preparation of the pure iridium and of the pure rhodium which were used in the recent determination of the freezing points of these metals at the National Bureau of Standards. His descriptions concerning the refining of these two metals supersede those given in a previous publication.<sup>28</sup>

A mixture of hydrazoic acid,  $\text{HN}_3$ , and hydrochloric acid, in water solution, was found by Franklin<sup>29</sup> to show properties of aqua regia to the extent that the solution dissolved platinum. Urmston and Badger<sup>30</sup> studied the photochemical reaction between bromine and finely divided platinum with light of wave-length shorter than 5000 Å and that longer than 5300 Å, as well as the thermal reaction from 0 to 25° C.

*Adsorption and Diffusion of Gases.* Sears and Becker<sup>31</sup> reported, in abstract form, that as the amount of platinum adsorbed on a tungsten surface increases, the thermionic activity decreases rapidly up to one layer, and then more slowly until at about ten layers it approaches platinum activity. McKinney<sup>32</sup> measured the adsorption of carbon dioxide and of carbon monoxide on palladium oxide over the temperature range -78 to 218° C. and found that adsorption of carbon dioxide is of the reversible physical type, whereas carbon monoxide shows physical adsorption at -78° and activated adsorption at higher temperatures, the apparent maximum for the latter at 350 mm. being at about 100° C. The isothermal absorption of hydrogen by palladium was studied by Krause and Kahlenberg<sup>33</sup> at temperatures ranging from 0 to 138° C.

Ferguson and Dubpernell,<sup>34</sup> in a study on overvoltage, published a paper on the mechanism of the transfer of electrolytic hydrogen and oxygen through thin sheets of platinum and palladium. Ham,<sup>35</sup> in one paper, reported the results of experiments on the diffusion of hydrogen through platinum, which checked those of Borelius and Lindblom,<sup>36</sup> and in another<sup>37</sup> those on diffusion through palladium. Harris, Jost, and Pearse<sup>38</sup> found that there was a ten-fold increase in the concentration of the heavier isotope, in a single step, when hydrogen was diffused through palladium under a 100-fold decrease in pressure, and concluded that the diffusion is an atomic process, and that there is an activation factor favorable

to the lighter isotope. Fink, Urey, and Lake,<sup>39</sup> from preliminary experiments, reported that with a palladium tube as cathode, fractionation of the two isotopes of hydrogen occurred, protium, the lighter isotope, diffusing through more readily.

In a paper concerning the shunt action of the electrolyte, when measuring the resistance of immersed and hydrogen-charged palladium wires, Smith<sup>40</sup> raises several objections to an explanation given by Knorr and Schwartz.<sup>41</sup> Somewhat later, Smith and Derge<sup>42</sup> investigated the rôle played by intergranular fissures in the occlusion and evolution of hydrogen by palladium and confirmed the conclusion, previously formed, that diffusion of hydrogen occurs primarily along slip-plane fissures, and only secondarily through the undistorted lattice. In a second paper, Smith and Derge<sup>43</sup> published an account of a study on the occlusion and diffusion of hydrogen in palladium and particularly of metallographic effects of gaseous hydrogen. Herzfeld and Goepfert-Mayer,<sup>44</sup> on the basis that hydrogen dissolved in palladium is apparently partially dissociated into protons and electrons, applied the concepts of the Debye-Hückel theory of electrolytic solutions, and by using Fermi statistics of the electrons, made a first-order calculation for the energy and conductivity.

*Catalysis.* Owing to the catalytic properties possessed by the metals of the platinum group, various investigators employed them in this capacity. Shepherd and Branham<sup>45</sup> used platinum in a critical study of the determination of ethane by combustion in excess oxygen, while Kobe and Arveson<sup>46</sup> studied the oxidation of hydrogen and of carbon monoxide over platinized silica gel, and later Kobe and Brookbank<sup>47</sup> used the same catalyst in experiments on the oxidation of methane hydrocarbons.

Heath and Walton<sup>48</sup> investigated the effect of salts on the catalytic decomposition of hydrogen peroxide by colloidal platinum.

Hammett and Lorch<sup>49</sup> determined the activation of hydrogen by bright electroplated platinum and iridium by measuring the polarization of electrodes carrying these catalysts, and in a subsequent article, Lorch<sup>50</sup> discussed the choice of catalysts of the hydrogen electrode and described the preparation of such electrodes plated with platinum black, bright platinum, and bright iridium. Kahlenberg, Johnson, and Downes<sup>51</sup> stated that a small portion of the hydrogen released from cathodically hydrogenated palladium reduces sulfur above 65° C.

McKinney and Morfit<sup>52</sup> have stated that platinum oxide is reduced by carbon monoxide at 0° C., and that the reaction is autocatalytic and has an induction period. In a subsequent paper, McKinney<sup>53</sup> reported that well-dried platinum oxide (PtO<sub>2</sub>) is reduced by carbon monoxide at 25° C. with an induction period of two hours, which period is shortened to thirty minutes at 40° C. He found, however, that if the platinum oxide is not dried at

110° C., or if moist carbon monoxide is used, reduction occurs at 0° C. with a short induction period.

Wiig<sup>54</sup> found that hydrogen and oxygen at low pressures reacted in the ratio of 2:1 by volume on platinum as a catalyst, when care was taken to eliminate any possibility of a change in concentration of the gaseous mixture due to differential diffusion.

Hartung and Crossley<sup>55</sup> employed a catalyst consisting of palladium on charcoal to reduce quickly and easily propiophenone to propylbenzene. The substitution of hydroxyl or methoxyl groups in propiophenone was found to influence the rate but not the extent of the reduction. A similarly prepared platinum catalyst proved to be inactive. In his studies on reduction of compounds in the morphine series, Small<sup>56-58</sup> and his co-workers used platinum oxide and also palladium as catalysts.

Andrews and Lowy<sup>59</sup> used a platinum catalyst in the reduction of azo-type compounds. Thomson<sup>60</sup> found that the acid oxidation products of olefins are the impurities which offset the poisoning effect of iron on platinum catalysts used in the reduction of olefins. Bjerrum and Michaelis<sup>61</sup> say that nitric oxide oxidizes leuco dyes in the presence of a little colloidal palladium.

Baldeschwieler and Mikeska<sup>62</sup> described the preparation of platinum oxide catalyst from spent material, using essentially the method of purification given by Wichers<sup>63</sup> for the preparation of pure platinum.

In a study of the reaction between nitrous oxide and hydrogen on platinum, Dixon and Vance<sup>64</sup> found that between 260 and 471° C. the rate is proportional to the partial pressure of nitrous oxide and nearly independent of that of hydrogen. The apparent energy of activation is 23,100 calories. Emmett and Harkness<sup>65</sup> noted the poisoning effect of activated adsorption of hydrogen on the para-ortho conversion of hydrogen at -190° C. over platinum, and consider this effect as constituting very strong evidence that the activated adsorption of hydrogen by platinum is in part at least a surface phenomenon.

*Electrochemistry.* Thews and Harbison<sup>66</sup> described the electrolytic plating of platinum on noble and on base metals, in connection with which they discussed technical details, endorsed the use of  $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ , and stated that platinum plating lasts longer than that of gold or silver. Experiments on the plating of rhodium from various types of baths were reported by Fink and Lambros<sup>67,68</sup> who concluded that the most satisfactory results were obtained with a bath containing 4 g. of rhodium per liter, 80 g. of sulfuric acid per liter, and 3 percent of ammonium sulfate, at 50° C. with a current density of 8 amperes per square decimeter.

McClain and Tartar<sup>69</sup> studied the effect of an electric field on the potential at a platinum-solution interface, while Steiner and Kahlenberg<sup>70</sup> measured the electric potential of platinum in nitric



acid. The electrode potentials of platinized platinum and of smooth platinum in mildly alkaline sugar solutions were measured by Ort and Roepke.<sup>71</sup>

Jones and Christian<sup>72</sup> measured the resistance and capacitance due to galvanic polarization with alternating current, using smooth platinum and platinized platinum electrodes. In another paper, Jones and Bollinger<sup>73</sup> discussed the various criteria as to quality and sufficiency of platinization in the measurement of the conductance of electrolytes.

Stareck and Taft<sup>74</sup> investigated the systems  $\text{Pt}/\text{AgNO}_3/\text{Pt}$ ,  $\text{Pt}/\text{KAg}(\text{CN})_2/\text{Pt}$ , and  $\text{Pt}/\text{KCN}/\text{Pt}$  with the aid of a modified Haring cell, while Bancroft and Magoffin,<sup>75</sup> using platinum electrodes, made a study of energy levels in a number of common reactions.

Using a platinum anode, and various metals as cathode, Topley and Eyring<sup>76</sup> studied the electrolytic separation of the hydrogen isotopes and discussed the mechanism of the cathode process.

**Physics. General Physical Properties.** Platinum-rhodium alloys containing approximately 10, 20, 40, 60, and 80 percent of rhodium were prepared by Acken,<sup>77</sup> who determined for each of these alloys the melting point, hardness, density, electrical resistivity, temperature coefficient of resistance, and the thermal electromotive force against platinum, while Wise and Eash<sup>78</sup> reported the results of investigations dealing with the tensile strength and annealing characteristics of platinum, palladium, and a number of their commercial alloys. Bridgman<sup>79</sup> measured, at pressures up to 12,000 atmospheres, compressibilities and pressure coefficients for rhodium at 30 and at 75° C., and for ruthenium at 0, 30, 75, and 95° C. Drier and Walker<sup>80</sup> found, by means of x-rays, that the gold-rhodium system consists of two solid solutions and that the solubility of rhodium in gold is between 4 and 8 atomic percent, whereas the solubility of gold in rhodium is between 1.1 and 2.5 atomic percent. They did not detect, however, any solubility of silver in rhodium or of rhodium in silver.

Using the Gouy method, Janes<sup>81</sup> measured the magnetic susceptibilities of a number of bi-, ter-, and quadrivalent palladium salts and found them to be diamagnetic.

Lawrence, Livingston, and Lewis<sup>82</sup> bombarded various targets, including platinum, with deutons having energies ranging from 600,000 to 1,330,000 volts. In addition to the emission of  $\alpha$ -particles, high-range protons were observed in large numbers. The emission of protons became unobservable when the deuteron energy was below 800,000 volts. A technic for evaporating platinum from a crucible, heated in a vacuum, by bombardment with electrons at 4000 volts produced from a tungsten filament, was described by O'Bryan.<sup>83</sup>

In an extensive paper<sup>84</sup> devoted to the equilibrium relationships

of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and oxygen, mention is made of the effect of crucibles of platinum and of rhodium on charges of magnetite, of volatilization of platinum and rhodium in oxygen, and of the consequent effect on thermocouples. In a general summary of the phenomenon of precipitation-hardening, Merica<sup>85, 86</sup> included a discussion of hardenable gold alloys containing silver, copper, platinum, and palladium. In a discussion of the use of frangible disks in pressure-vessel protection, Bonyun<sup>87, 88</sup> stated that platinum is a superior rupture-disk material.

*Crystal Structure.* Dickinson<sup>89</sup> published a paper on the crystal structure of tetramminepalladous chloride,  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , and West<sup>90</sup> reported an investigation on chloropentamminerhodium chloride,  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , concluding that the crystal structure of the isomorphous orthorhombic pentammines,  $[\text{R}(\text{NH}_3)_5\text{X}]\text{Y}_2$ , where R is Cr, Co, Rh, or Ir, and X and Y are halogens, is a distortion of the cubic structure of the hexammines,  $[\text{R}(\text{NH}_3)_6]\text{Y}_2$ .

Pauling and Huggins<sup>91</sup> reported the interatomic distances in crystals containing electron-pair bonds and listed the following compounds of the platinum metals:  $\text{RuS}_2$ ,  $\text{RuSe}_2$ ,  $\text{RuTe}_2$ ,  $\text{PdTe}_2$ ,  $\text{PtS}_2$ ,  $\text{PtSe}_2$ ,  $\text{PtTe}_2$ ,  $\text{OsS}_2$ ,  $\text{OsSe}_2$ ,  $\text{OsTe}_2$ ,  $\text{PdAs}_2$ ,  $\text{PdSb}_2$ ,  $\text{PtP}_2$ ,  $\text{PtAs}_2$ ,  $\text{PtSb}_2$ ,  $\text{Rb}_2\text{PdBr}_6$ ,  $\text{K}_2\text{PtCl}_6$ ,  $(\text{NH}_4)_2\text{PtCl}_6$ , and  $[\text{N}(\text{CH}_3)_4]_2\text{-PtCl}_6$ .

*Isotopes.* Bartlett<sup>92</sup> has discussed the prediction of isotopes and included reference to palladium, rhodium, ruthenium, iridium, and platinum.

Dempster<sup>93, 94, 95</sup> has reported the isotopic constitution of platinum, rhodium, palladium, and iridium. For platinum, he found isotopes of masses 192, 194, 195, 196, and 198 on analysis of the platinum ions from a high frequency spark, using a new spectrograph. Rhodium was reported to have an average atomic weight of  $102.92 \pm 0.03$ , with only a single isotope. Palladium was found to consist of six isotopes of masses 102, 104, 105, 106, 108, and 110, the four middle ones being about equally strong while the one at 110 was weaker and the one at 102 faintest of all. Using electrodes made of platinum-iridium alloy, Dempster found for iridium two isotopes, 191 and 193, the latter being definitely the stronger. Together with thallium and rhenium, this instance, according to Dempster, forms the third exception to the rule that the lighter of a pair of isotopes of an odd-numbered element is the more abundant.

*Spectra.* In the field of spectral analysis, Hansen and Stoddard<sup>96</sup> published a paper on a relation between the probability of excitation of line and continuous x-ray spectra of palladium. Allison<sup>97</sup> determined the line-widths of  $\text{K}\alpha_1$  and  $\text{K}\alpha_2$  for 14 elements from Fe to Ag, including ruthenium, rhodium, and palladium, with a double crystal spectrometer, and Williams<sup>98</sup> with Allison's apparatus, measured the full widths at half-maximum of the  $\text{L}\alpha_1$ ,  $\text{L}\beta_1$ ,

$L\beta_2$ , and  $L\gamma_1$  lines of platinum and iridium. Williams<sup>99</sup> also measured the relative intensities and transition possibilities of the *K*-series lines of ruthenium, rhodium, and palladium by the ionization-chamber method, and Ross,<sup>100</sup> using a double crystal spectrometer, studied the *K*-absorption discontinuity for these three metals. The radiated frequency and ionization potential of palladium were investigated by Kruger and Schoupp.<sup>101</sup> Purdom and Cork,<sup>102</sup> by means of a ruled grating, measured the x-ray emission wave-lengths in the *M*-series of 13 elements of higher atomic number than 71, including osmium, iridium, and platinum, and found that the results were consistently 0.32 percent higher than those found by the crystal method.

Richtmyer and Kaufman<sup>103</sup> examined for satellites the x-ray lines,  $La_1$  and  $La_2$ , of elements from Ta to U, including osmium, iridium, and platinum. Two satellites were found,  $La^{1x}$  extending from Au to U and  $La^x$  from Os to Bi. They also found that  $L\beta_2$  had two satellites, one extending from Ta to U, the other having a slightly greater range. In a subsequent paper, Hirsh and Richtmyer<sup>104</sup> attacked the problem of the origin of x-ray satellites by a study of their relative intensities under both cathode and fluorescent excitation. Among the elements studied were ruthenium, rhodium, and palladium. Kaufman<sup>105, 106</sup> reported the measurement of many weak lines in the *L*-spectra of iridium, platinum, and of osmium, and stated that many were diagram lines due to quadrupole radiation and that others were satellites of  $L\beta_2$ . Wilhelmy,<sup>107</sup> with a double crystal spectrometer, obtained quadrupole lines in the *K*-series of ruthenium. Goble,<sup>108</sup> in a paper mainly mathematical, discussed the four-vector problem and its application to energies and intensities in platinum-like spectra.

With the aid of a mechanical interval recorder, Albertson<sup>109</sup> found a number of energy levels of Os I, and in a subsequent paper<sup>110</sup> classified over 1050 osmium lines (of the arc spectrum) as transitions between 137 terms of Os I.

*Temperature Scales and Thermocouples.* The ratio of brightness of black bodies immersed in freezing iridium and freezing gold was determined directly, by Henning and Wensel,<sup>26</sup> in terms of the previously measured ratio of platinum to gold. With the freezing point of platinum previously established as  $1,773 \pm 1^\circ$  C., that of iridium was found to be  $2,454 \pm 3^\circ$  C. In a subsequent paper, Roeser and Wensel,<sup>27</sup> in a similar manner, determined the freezing point of rhodium as  $1,966 \pm 3^\circ$  C.

Southard and Milner<sup>111</sup> measured the resistance of platinum and of platinum-10 percent rhodium alloy between  $14^\circ$  and  $90^\circ$  K., with an estimated error of about  $\pm 0.02^\circ$ . They constructed a reference table of  $R/R_0$  for platinum between  $14^\circ$  and  $109^\circ$  K., giving values for each degree in this interval.

The thermal electromotive forces and the thermoelectric powers

of a series of platinum-rhodium alloys against pure platinum from 0° to 1200° C. were determined by Caldwell,<sup>112</sup> who also made comparisons between these values and those of several other investigators, the maximum difference found being of the order of 300 $\mu$ v. Roeser and Wensel<sup>113</sup> prepared reference tables for use with platinum to platinum-10 percent rhodium and with platinum to platinum-13 percent rhodium thermocouples. Through an interchange of platinum-platinum rhodium thermocouples and of specimens of silver between the National Physical Laboratory, the Physikalisch-Technische Reichsanstalt, and the National Bureau of Standards, an international comparison<sup>114, 115</sup> of temperature scales between 660 and 1063° C. was made, with an agreement to 0.1°. Roeser, Dahl, and Gowens<sup>116</sup> prepared tables giving the thermal electromotive force of chromel P against alumel, chromel P against platinum, and alumel against platinum at various temperatures in the range -310 to 2500° F. In establishing temperature scales for Cb, Th, Rh, and Mo, spectral emissivities were measured at  $\lambda=0.667\mu$  by Whitney,<sup>117</sup> who found, for rhodium, 0.242 between 1300 and 2000° K.

Roeser and Wensel<sup>118</sup> described various methods used for testing thermocouples and thermocouple materials, in particular the methods developed and used at the National Bureau of Standards, as well as precautions which must be observed to obtain various degrees of accuracy. Bradley,<sup>119</sup> in articles primarily for the practical man, gave information to users of thermocouples, while Brenner,<sup>120</sup> in a paper devoted to recent developments in platinum thermocouples, discussed the essential requirements, constancy of calibration and life, and mechanical strength of platinum-platinum rhodium thermocouples of high quality.

**Industry.** In an article of a popular nature, Wise<sup>121</sup> related the march of platinum in industry, while in another paper Wise and Eash<sup>122</sup> discoursed on the rôle of the platinum metals in dental alloys, treating particularly of the influence of platinum and palladium, as well as of heat treatment, upon the microstructure and constitution of these alloys. Harder<sup>123</sup> likewise, in a review, discussed the use of platinum and palladium in dentistry and in dental alloys. In a brief article, Carter<sup>123a</sup> discussed the hardening of platinum by means of iridium, osmium, and ruthenium. Hess,<sup>124</sup> in a popular article, included a brief description of the occurrence, distribution, and use of platinum. In a paper devoted to the geology of the beach placers of the Oregon Coast, brief reference is made by Pardee<sup>125</sup> to the occurrence of platinum, which is thought to have been carried from the interior, the original source, however, being not definitely known.

In a paper covering a survey of testing in the precious metal field, Wright<sup>126</sup> discussed the industrial, household, and personal uses of the platinum metals. Hoke<sup>127</sup> published the second edition

of a booklet, designed for the layman, on testing precious metals, which was reviewed by Wichers.<sup>128</sup>

Harbison<sup>129, 130</sup> stated, in a paper devoted to the plating of metals by palladium, that for satisfactory results the palladium should be plated on silver, copper, or a copper alloy, and that if it is to be plated on iron, zinc, or tin a coating of copper or of silver should first be applied.

From a critical study of precious metal catalysts for the oxidation of ammonia to oxides of nitrogen, Handforth and Tilley<sup>131</sup> concluded that platinum-rhodium alloys containing from five to ten percent of rhodium are the most advantageous and economical of any catalysts of this class thus far proposed.

A description of the silver refinery of the Raritan Copper Works at Perth Amboy, N. J., and of the recovery of platinum and palladium therein was given by Mosher.<sup>132</sup>

*Patents.* Wise<sup>133, 134</sup> was granted two patents on alloys containing 25 to 98 percent of palladium, 1 to 50 of copper, and 1 or more percent of silver, suitable for dental uses, electrical conductors, etc., and assigned them to the International Nickel Company, Inc. A foreign patent on palladium alloys was later taken out by the International Nickel Company.<sup>135</sup> Aderer<sup>136, 137</sup> likewise obtained patents on alloys for dental purposes, one for alloys containing 30 to 40 parts of gold, 35 to 50 of palladium, 10 to 23 of silver, 4 to 20 of copper, and 2 to 6 of zinc, the other for those containing 30 to 40 parts of gold, 35 to 50 of palladium, 18 to 30 of copper, and 2 to 6 of zinc. Holbrook<sup>138</sup> assigned to the H. A. Wilson Company his patent rights to alloys, suitable for electrical contacts or sparking points, containing 50 to 90 percent of osmium and 50 to 10 percent of rhodium. Taylor<sup>139, 140</sup> patented alloys suitable for dental work and jewelry formed of 25 to 65 percent of gold, 10 to 33 of silver, 2 to 25 of palladium, 10 to 25 of copper, and 0.5 to 5.0 percent of indium, and assigned the patents to Spyco Smelting and Refining Company. His second patent related to similar alloys which also contained 0.5 to 10 percent of platinum. Baker and Company, Inc.<sup>141</sup> was granted a foreign patent on alloys for jewelry, etc., containing 40 to 45 percent of palladium, 5 to 10 of platinum, 45 of silver, and 5 percent of nickel. Capillon and Carter<sup>142, 143, 144</sup> received three patents, assigned to Baker and Company, Inc., on alloys suitable for watch cases, electrical contacts, dentures, etc. The first patent covered alloys formed of palladium and platinum, 35 to 70 percent (of which amount 5 to 10 percent is platinum), and the remainder silver. The second patent related to similar alloys formed with nickel instead of with silver, and the third on the use of both silver and a nickel group metal with palladium and platinum.

Bart<sup>145, 146, 147</sup> took out one domestic and two foreign patents, assigned to the Precious Metals Developing Company, Inc., relat-

ing to the prevention of tarnishing of silver articles, such as tableware, prize cups, etc., by electroplating them with palladium and with rhodium. Baker and Company, Inc.<sup>148</sup> obtained a foreign patent for the electrolytic deposition of rhodium from a phosphate solution containing sulfuric acid. A similar domestic patent was also taken out by Zimmermann and Zschiegner<sup>149</sup> and assigned to Baker and Company, Inc. In another foreign patent, Baker and Company, Inc.<sup>150</sup> covered an electrolyte for rhodium plating made by heating an aqueous solution or suspension of a double nitrite of rhodium, such as  $(\text{NH}_4)_3\text{Rh}(\text{NO}_2)_6$ . Shields<sup>151</sup> was granted a patent on an electrolyte comprising an aqueous solution of a soluble rhodium salt, such as the sulfate or chloride, a soluble aluminum salt, such as potassium aluminum sulfate or aluminum chloride, and a free inorganic acid, such as sulfuric or hydrochloric acid. Wise<sup>152, 153</sup> likewise was granted patents on electrolytes, assigning them to the International Nickel Company, Inc., which covered, in one instance, a bath containing a soluble complex nitrite of a platinum group metal and to be operated within a range, 4:1 to 6:1, of nitrite to platinum metal, and in another instance, a bath containing an aminocyanide of platinum, palladium, or rhodium.

Ernst<sup>154</sup> obtained a patent, assigned to E. I. duPont de Nemours and Company, Inc., for a process of decorating ceramic surfaces with a palladium-gold alloy.

Ridler<sup>155, 156, 157</sup> was granted three patents, assigned to the Grasselli Chemical Company, on the regeneration of spent platinum catalysts, used in the oxidation of sulfur dioxide, by means of allyl alcohol, formaldehyde, oxalic, acetic, and formic acids.

Tilley and Whitehead<sup>158</sup> of E. I. duPont de Nemours and Company, Inc., were given a patent on a catalyst for the oxidation of ammonia, formed of alloys of platinum and rhodium having a solid surface of platinum, while Hickey,<sup>159</sup> assigning his rights to J. Bishop and Company, patented an alloy of platinum, rhodium, and cobalt to be used in the form of gauze as a catalyst for the oxidation of ammonia.

Rodrian<sup>160</sup> obtained a patent on a process for the recovery of gold and platinum from ores. Wise and Vines<sup>161</sup> were granted a foreign patent, assigned to the International Nickel Company, Inc., for the metallurgical recovery of precious metals from nickel-copper mattes.

Woodward<sup>162</sup> assigned to Kastenhuber and Lehrfeld his patent rights to an apparatus, used in the manufacture of pen points, for shattering molten platinum alloys into drops by the action of a revolving disk.

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# Chapter XI.

## Electro-organic Chemistry.

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The most notable advances in electro-organic chemistry during the past several years have been made in the development of new electrolytes for oxidation and reduction of organic compounds, in research on the electrolysis of organo-metallic compounds, and on the electrodeposition of metals from non-aqueous solutions and from organic electrolytes.

Some of the more important phases of electro-organic chemistry before 1932 have been reviewed by Brockman.<sup>1</sup> This chapter will, therefore, include material published after this review.

**Electrolysis of Aliphatic Acids (Kolbe Synthesis).** Wallis and Adams<sup>2</sup> have shown that the 3,4-dimethylhexane formed in the electrolyses of both *d*- and *l*-potassium methylethylacetate is optically inactive.

The electrolysis of aliphatic acids of the ammonia system has been studied for the first time by Fulton and Bergstrom.<sup>3</sup> They found that potassium acetamidine in liquid ammonia yielded ethane in a manner similar to its formation from potassium acetate in aqueous or alcoholic solutions. Higher homologous amidines yielded mixtures of methane and ethane, due to deep-seated decomposition. It is interesting to note that high current densities are necessary for a successful Kolbe synthesis in liquid ammonia just as in aqueous solution.

Petersen's preparation of tetracontadiene by the electrolysis of potassium oleate was repeated by Dover and Helmers.<sup>4</sup> They were unable to obtain the completely pure product described by Petersen.

**Electrolytic Oxidation.** Rasch and Lowy<sup>5</sup> have carried out the electrolytic oxidation of anthraquinone to hydroxyanthraquinones at a platinum gauze anode in a concentrated sulfuric acid electrolyte.

Leucobases of triphenylmethane dyes have been oxidized to the color-bases electrolytically by G. H. White, Jr., with Lowy.<sup>6</sup> Both acid and alkali soluble materials have been studied. A platinum gauze anode was used. Contact between the anode and the depolarizer was made by pressing a paste consisting of leucobase and carbon into the anode. The compounds used were the leuco-bases of

Malachite Green, Brilliant Green, Guinea Green, and Brilliant Blue. The colors obtained by the electrolytic oxidation of Malachite Green, Brilliant Green, and Guinea Green compare favorably with those resulting from the customary lead dioxide oxidation.

The electrolytic oxidation of naphthalene to  $\alpha$ -naphthoquinone has been studied by E. G. White with Lowy<sup>7</sup> in acid solution. The anode was made up by the method described in the preceding paragraph.

McKee and Brockman<sup>8</sup> found it impossible to oxidize benzene or toluene to phenols in the aromatic sulfonate electrolytes which were so successful in the reduction of nitro to azo compounds (described under the section on reductions).

McKee and Heard<sup>9</sup> have made further studies of electrolytic oxidations in sulfonate solutions. They have been able to oxidize benzyl alcohol and benzaldehyde to benzoic acid in good yields. An interesting observation made by the investigators was that these oxidations could be catalyzed by copper and manganese oxides and by nickel and cobalt hydroxides but not by cerium hydroxide. The best results were obtained with nickel hydroxide.

In a subsequent paper<sup>10</sup> the authors have studied the oxidation of a wide variety of organic compounds. Hydroquinone was oxidized to quinhydrone. The linseed fatty acids showed an oxygen absorption efficiency of 92 percent. There is some evidence that hydroxylation of the double bonds takes place during this oxidation. Benzoin was oxidized to benzoic acid in good yield. Toluene, naphthalene, anthracene, and borneol underwent no oxidation.

It was found that nickel anodes could be used without corrosion in alkaline solutions of the sulfonates. This makes it possible to carry out oxidations at a comparatively low oxygen overvoltage and thus avoid oxidizing the depolarizer to carbon dioxide and water. Since no organic solvent is necessary for blending the depolarizer with the electrolyte the efficiency of oxidation in these solvents is enhanced due to the fact that all of the oxygen may be absorbed by the depolarizer. Under neutral or alkaline conditions the sulfonates are unattacked by anodic oxygen.

A patent has been granted to Youtz<sup>11</sup> for the electrolytic hydroxylation of ethylene to ethyleneglycol in caustic soda solution.

**Reactions of Organic Compounds with Products of Electrolysis.** Isbell, Frush and Bates<sup>12</sup> have continued their work on the oxidation of dextrose to calcium gluconate. The oxidation is brought about by bromine liberated at the anode in the electrolysis of calcium bromide. The method has been found very satisfactory for the production of large quantities of calcium gluconate. Helwig<sup>13</sup> has been granted a patent for the electrolytic separation of aldoses from ketoses, in which the aldoses are oxidized in a similar manner. Magnesium xylonate<sup>14, 15</sup> has been prepared from xylose in the manner described above, except that magnesium ion was substi-

tuted for calcium ion. The yields are excellent. Cook and Major<sup>16</sup> have succeeded in preparing calcium 5-ketogluconate from glucose by the electrolytic method.

Hockett<sup>17</sup> has prepared strontium xylonate in excellent yield by the electrochemical oxidation of xylose.

McKee and Heard<sup>10</sup> have attempted the electrolytic halogenation of toluene in sodium xylenesulfonate solution. They found that both the toluene and the solvent were halogenated simultaneously.

The electrochemical nitration of naphthalene has been studied by Calhane and Wilson<sup>18</sup> and optimum conditions determined for the formation of nitronaphthalene.

Kirk and Bradt<sup>19</sup> have carried out a research on the electrochemical nitration of toluene for the first time. Both nitration and oxidation took place. It was found that certain metal salts catalyzed the nitration.

**Electrolytic Reduction of Nitro and Nitroso Compounds.** A number of patents have been taken out on the electrolytic reduction of nitro compounds. Jewett<sup>20, 21</sup> has been granted two patents covering apparatus for this type of reduction.

Cupery<sup>22</sup> has found that nitro compounds may be successfully reduced to amines if the oxygen of the air is kept out of the cathode compartment by hydrogen chloride gas.

Fieser and Martin<sup>23</sup> have used the method of Gattermann successfully for the electrolytic preparation of 4-amino-5-hydroxy-, 4-amino-7-hydroxy- and 1-methyl-4-nitro-7-hydroxy-benzothiazoles from the corresponding nitro compounds.

The same authors have also carried out the reduction of 5(8)-nitroisoquinoline<sup>24</sup> to 5(8)-amino-8(5)-hydroxyisoquinoline by the same procedure.

Brigham and Lukens<sup>25</sup> have made a thorough study of the electrolytic reduction of nitrobenzene to *p*-amidophenol.

Kerns<sup>26</sup> has determined the optimum conditions for the electrolytic preparation of azoxybenzene from nitrobenzene.

McKee and Brockman<sup>8</sup> have discovered that concentrated aqueous solutions of the sodium and potassium salts of aromatic sulfonic acids will dissolve large quantities of organic compounds and may, therefore, be used as electrolytes for reductions, obviating the use of a blending agent for putting the organic depolarizer into solution.

In this medium the authors have carried out the reduction of many aromatic nitro compounds to the azo stage in excellent yield; the sulfonate bath becomes mildly alkaline as electrolysis proceeds. A phosphor bronze cathode was found superior to copper or nickel. McKee and Gerastopolou<sup>27</sup> have extended this work to include reductions to hydrazo compounds and amines in acid solution. The reductions to hydrazo compounds were particularly successful both in laboratory size and large size equipment.

Alles<sup>28</sup> found that the electrolytic method was superior to others for the reduction of certain phenylnitropropylenes to *dl*- $\beta$ -phenylisopropylamines.

Cook and France<sup>29</sup> have succeeded in preparing *N*-amidoisindoline in excellent yield by the electrolytic reduction of *N*-nitrosoisindoline.

**Electrolytic Reduction of Carbonyl Compounds.** Swann<sup>30</sup> has determined the optimum conditions for the electrolytic reduction of methylpropyl ketone to pentane at a cadmium cathode in aqueous sulfuric acid. Swann and Feldman<sup>31</sup> have studied the effect of other common metal cathodes under the same experimental conditions. Cadmium, zinc, lead, and mercury cathodes caused the highest yields of hydrocarbon. Swann, Deditius, and Pyhrr<sup>32</sup> have compared the behavior of sulfuric-glacial acetic acid to aqueous sulfuric acid as an electrolyte in this reduction. They showed that the yields of pentane at different common metal cathodes corresponded more closely with the hydrogen overvoltage of the cathode in glacial acetic acid than in aqueous solution. The yields in the two media differed markedly but were of the same order of magnitude.

Very small amounts of iron were found by Swann<sup>33</sup> to lower the yield of benzopinacol resulting from the electrolytic reduction of benzophenone at an aluminum cathode in acid solution.

The electrolytic reduction of benzophenone in glacial acetic acid has been studied by Swann.<sup>34</sup> It was found that benzopinacol is the main product in both aqueous and glacial acetic-sulfuric acid solution, but that it undergoes rearrangement to the pinacolone in the acetic acid electrolyte. An iron cathode gives the best results. Even though the hydrogen overvoltages in glacial acetic acid solution are much higher than in water, reduction does not go to completion.

The electrolytic reduction of acetophenone in acid solution has been studied at all the common metal cathodes by Swann and Nelson.<sup>35</sup> The main products are acetophenone pinacol, bis-( $\alpha$ -methyl)-benzyl ether, and a resin of unknown constitution. The best yield of pinacol occurred at a lead cathode.

Kyrides<sup>36</sup> has used the electrolytic method for the preparation of 3-methylpentane-2,4-diol from 3-methylpentane-4-ol-2-one.

Creighton<sup>37</sup> has improved his process for the electrolytic reduction of sugars to alcohols in alkaline solution by changing the mercury cathode formerly used to amalgamated lead. This process is now operating industrially.

Kyrides and Bertsch<sup>38</sup> have carried out the electrolytic reduction of maleic to succinic acid at a lead cathode in a benzenesulfonic acid electrolyte in high yield.

Muskat and Knapp<sup>39</sup> have shown that vinylacrylic acid, when reduced in a sodium chloride electrolyte, undergoes 1,4 addition of hydrogen to give  $\Delta^2$ -pentenic acid.

McKee and Brockman<sup>8</sup> obtained high yields of benzoin by the electrolytic reduction of benzil in sulfonate solvents.

Cook and France<sup>29</sup> have studied the electrolytic reduction of phthalimide, phthalimidine, methylphthalimide and methylphthalimidine at several of the common metal cathodes of high hydrogen overvoltage. The best yields of isoindolines were obtained at lead and cadmium cathodes.

Craig,<sup>40</sup> using the method of Tafel and Stern for the electrolytic reduction of succinimides together with a method for the continuous extraction of the catholyte by chloroform, has succeeded in obtaining high yields of *N*-methyl- $\alpha$ -pyrrolidone from *N*-methylsuccinimide.

**Electrolytic Reduction of Miscellaneous Nitrogen Compounds.** Cook and France<sup>41</sup> have studied the electrolytic reduction of *o*-, *m*-, and *p*-tolylidiazonium chlorides to the corresponding hydrazines. Satisfactory yields were obtained only at a mercury cathode. The highest yield was obtained with the *ortho*-compound, while the *para*-compound yielded the least hydrazine.

Wenker<sup>42</sup> has reported some excellent yields of benzylamines in the electrolytic reduction of imido ethers.

Small and Lutz<sup>43</sup> have prepared dihydrodesoxycodine-B in nearly quantitative yields by the electrolytic reduction of desoxycodine-C. They have also used the electrolytic method to reduce pseudocodeine to dihydropseudocodeine-B.<sup>44</sup>

Morris and Small<sup>45</sup> have used the electrolytic method in alkaloid researches to reduce  $\delta$ -ethylthiocodine-A to dihydro- $\delta$ -ethylthiocodine-A and dihydrodesoxycodine. The electrolytic method was unsuccessful in the reduction of  $\alpha$ - and  $\beta$ -ethylthiocodines.

**Electrolytic Dehalogenation.** Hood and Imes<sup>46</sup> have shown that the maximum current efficiency in the electrolytic reduction of chloroacetic acid to acetic acid occurs at a lead cathode.

**Electrolysis of Organometallic Compounds.** Overcash and Mathers<sup>47</sup> have found that dimethylaniline gives the best results as a solvent in the electrodeposition of magnesium from Grignard compounds. Evans and Lee<sup>48</sup> have studied the anode products in the electrolysis of Grignard compounds in ether. They found that ethylmagnesium halides yielded ethane and ethylene and that propyl compounds yielded propane and propylene. Traces of hydrogen were always found. A mixture of ethyl and phenyl Grignard compounds yielded only ethane. In concentrated solution methylmagnesium halides yielded ethane as the main product. In more dilute solutions methane and olefins appeared. The authors suggest a mechanism for these reactions. Evans, F. H. Lee, and C. H. Lee<sup>49</sup> have determined the discharge potentials of anions in the electrolysis of Grignard compounds in ether. The anions listed in order of descending potential are: phenyl-, methyl-, propyl-, butyl-, ethyl-, isobutyl-, isopropyl-, *tert*-butyl-, and allyl-. Adams<sup>50</sup> compares the above results to those of Derick<sup>51</sup> on the ionization constants of aliphatic acids and points out that the effect of

substituting methyl groups in the  $\alpha$ -position has the same effect on the decomposition potentials of the Grignard reagents as on the logarithms of the ionization constants of organic acids.

Keyes, Phipps, and Klabunde<sup>52</sup> have patented the method for electrodepositing aluminum from tetra-alkyl ammonium bromide-aluminum bromide solution.

A patent has been taken out by Keyes and Swann<sup>53</sup> on the electrodeposition of aluminum from Grignard type compounds in ether. Blue and Mathers<sup>54</sup> have found that aluminum can be electroplated successfully from solutions prepared by allowing aluminum-Grignard compounds to react with aromatic hydrocarbons in the presence of aluminum bromide. The bath conducts current without the addition of any solvent.

Foster and Hooper<sup>55</sup> have electrolysed sodium triphenyl germanide in liquid ammonia. The anode products are hexaphenyldigermane, triphenylgermane, and nitrogen. At a platinum anode the quantity of nitrogen corresponds roughly to the amount of triphenylgermane produced; at mercury it is markedly smaller.

**The Electrodeposition of Metals from Non-Aqueous Solutions and from Organic Compounds in Aqueous Solution.** Stillwell and Audrieth<sup>56</sup> have electrodeposited arsenic, antimony, and bismuth from their chlorides in glacial acetic acid. It was found that, under the experimental conditions used, the electrodeposited arsenic was always amorphous, while the bismuth was crystalline. Depending on conditions of temperature and concentration, antimony was deposited in the metastable or in the crystalline form. The authors point out that the solvent must be considered as an additional important factor among the conditions which affect the structure of electrodeposited antimony.

Blue and Mathers<sup>57</sup> have succeeded in electrodepositing aluminum as an alloy with iron from a solution of their chlorides in formamide. Aluminum would not deposit in a pure state under these conditions. The electrodeposition of other metals was studied from both chloride and sulfocyanate solutions in formamide, but the results were in general inferior to those obtained in aqueous solution.

Meints, Hopkins, and Audrieth<sup>58</sup> have continued their work on the electrolytic preparation of rare earth amalgams in non-aqueous solvents. In this paper they describe the electrodeposition of lanthanum from the chloride in ethyl alcohol. Jukkola with Audrieth and Hopkins<sup>59</sup> has extended this work to include neodymium, cerium, samarium, and yttrium. Experimental details of the electrolytic preparation of rare earth alloys are given in a paper by Hopkins and Audrieth.<sup>60</sup>

Fink and Young,<sup>61</sup> in a paper on the electrodeposition of cadmium-zinc alloys, point out that the function of an addition agent is not necessarily confined to preventing the growth of large crystals but may also affect the proportion of the metal ion being deposited

by forming a complex with it. They found that the only successful addition agents in their work were organic nitrogen compounds. Since it is known that cadmium forms complexes with such compounds and the corresponding zinc complexes are not found in the literature, the authors assumed that the cadmium formed complexes, while the zinc did not, with the effect that the proportion of zinc increased in the alloy plate in the presence of these addition agents.

Calbeck<sup>62</sup> has been granted a patent on an electrolytic cell suitable for the deposition of sponge lead and lead peroxide from lead acetate solution.

**Electrothermal Processes in Organic Chemistry.** Dow<sup>63</sup> has patented a process for the production of carbon disulfide by passing sulfur vapor over charcoal which has been heated to reaction temperature by an electric current passing through the charcoal and conducting carbon.

Acetylene and other products have been produced by Nutting and Rowley<sup>64</sup> in the thermal decomposition of a hydrocarbon oil by an electric arc.

The electric arc has been used by Jakosky<sup>65</sup> in the production of carbon black by the thermal dissociation of hydrocarbon liquids.

Williams<sup>66</sup> has been granted a patent for converting benzene to biphenyl in an electric furnace.

Strosacker and Schwegler<sup>67</sup> have taken out a patent on the preparation of tetrachloroethylene and hexachloroethane by allowing carbon tetrachloride to come into contact with electrically heated carbon.

**Miscellaneous Industrial Applications of Electro-Organic Chemistry.** Cellulose has been bleached by passing it near an anode in a sodium chloride solution by Seavey, Phillips, and Olsen.<sup>68</sup>

The anode process for the electrodeposition of rubber is discussed by Beal<sup>69</sup> and by Hirsch.<sup>70</sup> The following topics are taken up: electrodeposition on metals, electrodeposition on permeable materials, anode ionic deposition, the processing of deposits, and commercial applications.

Watson<sup>71</sup> has described a successful method for decreasing salts in whey protein (lactalbumin) by electrodialysis. Lima<sup>72</sup> has been granted a patent on the purification of sugar-containing liquids. The method consists in electrolysis between aluminum electrodes. The aluminum is attacked and forms salts with the acids of the liquor. These may be removed by charcoal treatment. Hazzid<sup>73</sup> has isolated the sulfuric acid ester of galactan in an impure state by the electrodialysis of its sodium salt.

Roberts<sup>74</sup> has patented a process for breaking emulsions by subjecting them to repeated action of magnetism at different frequencies. Hanson<sup>75</sup> and van Loenen<sup>76</sup> have taken out patents on the electrical dehydration of petroleum emulsions. In order to



improve the efficiency of dehydration of emulsions natural gas is forced into the emulsion under pressure by Eddy.<sup>77</sup> A patent has been granted to Harlow<sup>78</sup> for the electrostatic removal of pitch from gases such as coal gas or producer gas.

A method for preparing catalysts for hydrogenating hydrocarbon oils has been patented by Weber.<sup>79</sup> The hydrocarbon material is mixed with sodium chloride or a caustic alkali solution and electrolysed between electrodes of iron, chromium, or tungsten. The electrodes are attacked and the products formed act as hydrogenating catalysts.

**Electrical Discharge Through Organic Compounds.** Jaeger<sup>80</sup> has been granted a patent for the decarboxylation of organic dibasic acids to monobasic acids by electronic discharge at high temperatures.

Hillis<sup>81</sup> has patented a process for synthesizing liquid hydrocarbons from gaseous aliphatic hydrocarbons by subjecting the gases first to cathode and x-rays and then subjecting them to a mercury vapor arc discharge under pressure in the presence of powdered nickel. The latter acts as a dehydrogenating catalyst.

Thornton and Burg with Schlesinger<sup>82</sup> have found that dichlorodifluoromethane, while very stable to heat treatment, undergoes decomposition in the high tension electrical discharge to a variety of products.

**Voltaic Cells with Organic Electrolytes.** Bent and Gilfillan<sup>83</sup> have measured for the first time the electromotive force of galvanic cells containing alkali metal derivatives of triphenylmethyl as the electrolyte in ether. They found that, when potassium amalgams are used for both electrodes, the cells give potentials which might be expected for normal salts, while if one electrode is pure potassium the potentials are erratic. The erratic behavior of the latter cell is due to some change in the electrolyte which takes place in the presence of potassium.

**Organic Dielectrics.** The behavior of dielectrics as insulators is engaging the attention of a number of investigators. Race<sup>84</sup> has found that the longer the time of heating a mineral insulating oil with air, the greater the increase in conductivity when the oil is heated to high temperature. He also found that oxidation increases the high frequency dielectric losses but does not affect the frequency at which the maximum loss in each sample occurs.

The conductivities of synthetic resins and varieties of wood as a function of the temperature have been determined by Clark and Williams.<sup>85</sup>

A symposium on dielectrics was held by the Electrochemical Society in 1934. The papers on organic dielectrics follow. The first paper was by Barringer,<sup>86</sup> who discussed the relation between chemical and physical structure and dielectric behavior from a practical point of view. Whitehead<sup>87</sup> pointed out that dielectric loss

in insulating liquids is to a great extent due to conduction. Some general properties of liquid organic dielectrics were discussed by Karapetoff.<sup>88</sup> Clark<sup>89</sup> described new synthetic liquid dielectrics. Pentachlorodiphenyl, a liquid with a pour point of 10° C., is superior in many ways to hydrocarbon insulating oils in its stability to heat and oxidation. This compound when mixed with the proper proportion of trichlorobenzene has excellent properties as a transformer oil. The pour point is lowered to -18° C. with accompanying drop in viscosity. A voltage-time study of the failure of rubber compound insulation has been made by Mason.<sup>90</sup> Alkyd-resins as dielectrics have been discussed by Kienle and Race.<sup>91</sup> Finally, Morgan<sup>92</sup> has studied the dielectric behavior of halowax and paper, and glycerine.

The dielectric constant of cellophane has been studied by Stoops,<sup>93</sup> it has been found to be nearly twice that of cellulose acetate.

Clark<sup>94</sup> has found that chemical changes resulting in an increased power factor and decreased dielectric strength result from heating cellulose insulation to temperatures higher than 100° C.

White<sup>95</sup> has pointed out that the maximum dielectric loss factor in a polar substance increases with decreasing temperature while in a heterogeneous mixture the maximum decreases with decreasing temperature.

The progress in dielectric research for 1934-1935 has been reviewed by Whitehead.<sup>96</sup>

**Oxidation-Reduction Potentials of Organic Compounds.** Research in the field of oxidation-reduction potentials is always adequately covered in the chapters on analytical, organic, and biochemistry and will, therefore, not be discussed here.

**Organic Depolarizers.** Hunter and Stone<sup>97</sup> have measured the potentials of several depolarizers against different cathodes. They found that the order of sequence of the potentials at a series of cathodes was the same regardless of the depolarizer, but that the magnitude of the potential changed with different depolarizers. The order of sequence of the potentials is related to the work function of the cathode, while the magnitude of the potential at any given cathode is related to the electron affinity of the depolarizer.

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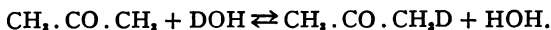
## Chapter XII.

### Aliphatic Compounds.

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For the sake of simplicity of presentation, the subject matter published during the year is discussed under separate topics. A discussion of the results by the reviewers, while eminently desirable, was made impossible by the number of topics and lack of space. It is hoped, however, that the arrangement used and some of our comments will give the reader an adequate idea of the trends of research in the chemistry of aliphatic compounds.

**Deuterium Compounds.** By far the most interesting work with deuterium involves the isotopic exchanges, particularly those carried out at ordinary temperatures. We may as well begin our review with the polemical papers; an indication that the analytical methods have not yet reached a high degree of precision, or are not sufficiently standardized. Thus, in last year's *Journal of the American Chemical Society*, it was reported that an isotopic interchange takes place between heavy water and acetylene in alkaline solution.<sup>1</sup> This year that claim is contested. No interchange is reported even under conditions more drastic than those previously described.<sup>2</sup> The senior author of the first publication, however, reaffirms his previous position, and records preliminary data on equilibrium studies at different temperatures and pressures. A mass spectrograph analysis of the acetylene produced under one set of equilibrium conditions indicated ten percent of  $C_2HD$  in the gas mixture.<sup>3</sup> There is little doubt now that the hydroxyl hydrogen atoms of carbohydrates can be replaced by deuterium merely by dissolving the substances in different concentrations of  $D_2O$ .<sup>4</sup> Ten carbohydrates were studied and in each case the exchange number coincides with the number of hydroxyl groups in the molecule. A more complete study of the kinetics and equilibrium of the isotopic exchange was made in the case of acetone.<sup>5</sup> Alkali was used as the catalyst, and under those conditions the exchange is reversible:



It is of interest in this connection to recall that treatment of benzene with  $D_2SO_4$  (90 percent) at room temperature resulted in an exchange

of H for D, and that some substituted benzenes exchanged nuclear H for D more readily.<sup>6</sup>

A few preliminary papers on heterogeneous catalysis in the exchange of deuterium and the hydrogen in methane have appeared. Considerable formation of mixtures of deuteriomethanes\* is observed by exposing methane and deuterium to the action of excited mercury<sup>7</sup> at temperatures from 40° to 300°, as well as under the influence of a reduced nickel catalyst at 184-305°.<sup>8</sup>

Acetylene and deuterioacetylene (acetylene-d<sub>2</sub>) polymerize at equal rates under the influence of Rn  $\alpha$ -rays,<sup>9</sup> but differ considerably in the mercury photosensitized polymerization.<sup>10</sup> The rate of polymerization is 30 percent greater with acetylene than with deuterioacetylene, over a considerable pressure range.

In the homogeneous reaction at 524° and 560°, hydrogen and deuterium combine with ethylene at the same rate,<sup>11</sup> while heterogeneous catalysis rates with Cu indicated a rate ratio, H<sub>2</sub>/D<sub>2</sub>, of 1.59.

The preparation of pure deuteriochloroform is described.<sup>12</sup> The properties closely resemble those of ordinary chloroform.

**Saturated Aliphatic Hydrocarbons and Alkyl Halides.** A great deal of work was done in this field by both organic and physical chemists. Unfortunately, neither a consolidation of the old positions nor a distinct advance has been made. No new facts, but a few improvements in methods of preparation and a few more (presumably) exact measurements of properties and interactions of molecules, are recorded. The general picture, however, appears about as "blurred" as before.

Perhaps the most interesting reaction described is the interaction of paraffin and olefin hydrocarbons in the presence of the halides of Al, B, Be, Ti, Zr, Hf, Th, Cb, and Ta as catalysts, and under otherwise mild conditions.<sup>13</sup> The alkylation of benzenoid hydrocarbons by paraffin hydrocarbons in the presence of a catalyst is of interest. Thus, it is stated that 2,2,4-trimethylpentane reacts with benzene in the presence of aluminum chloride and zirconium chloride as catalysts to yield a mixture of isobutane and di-*tert*-butylbenzenes.<sup>14</sup>

The hydrolysis of secondary and tertiary aliphatic halides has been studied. Two papers deal with the action of inorganic bases on isobutyl bromide and on tertiary amyl halides (chloride and bromide). The effects of bases (KOH, NaOH, AgOH, and water) on isobutyl bromide were studied under varying conditions of temperature and concentration. Olefin yields of 10.8-65.5 percent were obtained, depending upon the temperature and concentration of alkali, while the rate of reaction is greater in more dilute solution.<sup>15</sup> The same factors influence the amount of olefin formation in the case of the tertiary amyl halides and the percentage of olefin

\* For the infrared absorption spectra of methyl deuteride see N. Ginsburg and E. F. Barker, *J. Chem. Phys.*, 3: 668 (1935).

formation is dependent upon the nature of the base.<sup>16</sup> The hydrolysis of secondary and tertiary alkyl halides is unimolecular and independent of reagent anions. A mechanism of hydrolysis is postulated.<sup>17</sup>

The thermal decomposition of pentane mixed with steam was investigated at temperatures of 600-800°. Cleavage of the molecule took place, yielding all possible isomers, saturated and unsaturated. The variation of conditions that affects the yield of ethane, ethylene, and hydrogen is discussed.<sup>18</sup> The isomerization of heptane with aluminum chloride is claimed to yield about one percent of hexane and four percent of 2-methylhexane, and no other isomers.<sup>19</sup>

Adequate synthetic methods for the preparation of hexadecane,<sup>20</sup> hexadecyl iodide,<sup>21</sup> 1,5-dibromopentane,<sup>22</sup> and dodecyl bromide<sup>23</sup> are described. The use of alkyl bromides and sodium sulfite (Strecker reaction) has been extended to the preparation of sulfonic acids of octane, decane, dodecane, tetradecane, hexadecane, and octadecane.<sup>24</sup>

A procedure for the classification of hydrocarbons is described.<sup>25</sup> It is based upon miscibility with nitromethane, aniline, and benzyl alcohol; bromate-bromide titration; and upon the usual constants (melting point, boiling point, and density). A tabulation of the number of calculated isomers of the simple aliphatic compounds has appeared.<sup>26</sup>

A discussion of the mathematical papers dealing with the electronic structure of polyatomic molecules and energies of hydrocarbon molecules is out of place in this review. Brief mention is made of this work in case it is not treated in some more appropriate chapter. The energies of a number of hydrocarbon molecules have been calculated by the Heitler-London-Pauling-Slater method. In spite of the agreement of calculated and experimentally determined values, the validity of the additivity rule is questioned.<sup>27</sup>

The ionization potentials of ethane, ethylene, and acetylene are interpreted in terms of the electron configuration. Of considerable interest is the treatment by the author of "reduced" interatomic distances. These are studied as a measure of overlapping of orbitals of different atoms.<sup>28</sup> Spectroscopic data have also been used in the calculation of the heat capacity of methane and the four chloromethanes. It is claimed that these figures are more reliable than the thermal data.<sup>29</sup> A new type of "stereoisomerism," in which the two ethyl groups of butane rotate around the central C-to-C bond, is discussed in a mathematical paper.<sup>30</sup>

The mechanism of the oxidation of a few hydrocarbons with oxygen has been studied. In the case of methane the limiting pressure of low pressure explosion mixtures depends upon the surfaces used.<sup>31</sup> An induction period in the oxidation of propane has

been demonstrated, and a study made of the effect of surfaces on the reaction.<sup>32</sup> The oxidation of propane by oxygen is assumed to be a chain reaction, with the free radicals, propyl ( $\text{C}_3\text{H}_7$ ) and methoxyl ( $\text{CH}_3\text{O}$ ), as the chain carriers. The primary products of oxidation are: formaldehyde, methanol, carbon monoxide, and water.<sup>33</sup> The intermediate peroxide formation in the oxidation of chloroform by oxygen of air is postulated. The peroxide presumably decomposes to yield phosgene and hydrogen chloride.<sup>34</sup> A study on the oxidation of iodoform solutions has been reported.<sup>35</sup>

The question of methylene *versus* methyl radicals in the decomposition of methane is again in the foreground. The validity of the conclusion drawn from the removal of tellurium mirrors is questioned, and the view is again put forward that the kinetics of the decomposition are inconsistent and incompatible with any mechanism involving methyl radicals, but in good agreement with the methylene mechanism.<sup>36</sup>

A number of papers, photochemical and others, deal with the halogenation of aliphatic compounds, and the effect of different radiations on the decomposition of organic halides.

The chlorination of propane in the homogeneous reaction has been shown to be of the chain type (induction period, inhibitory oxygen effect, reduction of rate by packing, and explosions).<sup>37</sup> The chlorination over catalysts was also studied.<sup>38</sup> The formation of 1,2-dichloropropane was shown to be due to the addition of chlorine to propylene, formed by pyrolysis of propyl chloride. In the photochlorination of pentane in the liquid phase, with light at 3650 Å, the reaction is proportional to the first power of chlorine concentration.<sup>39</sup> The quantum efficiency is  $192 \pm 14$  at 25°.

Carbon tetrachloride is stable to light of 2537 Å. In the presence of oxygen, however, the reaction is assumed to take the following course:<sup>40</sup>  $2\text{CCl}_4 + \text{O}_2 \rightarrow 2\text{COCl}_2 + 2\text{Cl}_2$ . The chlorine-sensitized photochemical oxidation of chloroform leads to phosgene and hydrogen chloride. The quantum efficiency is about 100 moles of chloroform oxidized per einstein of radiation absorbed.<sup>41</sup>

The photobromination of tetrachloroethylene is accelerated by small amounts of oxygen. With large amounts of oxygen as in the case of chloroform, the halogen-sensitized oxidation begins to play an important rôle, with a consequent drop in the rate of bromination.\* Mixtures of liquid chloroform and liquid bromine react when illuminated with light of 2650 Å in the presence of oxygen, but not otherwise.<sup>42</sup> The effect of wave-lengths of 4358, 5461, 5770, and 5790 Å on the iodine-sensitized decomposition of ethylene iodide in solution at 76.6° gave<sup>43</sup> rate constants of 1:0.931:0.861.

The absorption spectra of *cis*- and *trans*-dichloroethylenes have been

\* It is unfortunate that the accelerating effect of HBr on the addition of bromine to ethylenic compounds is not taken into account or discussed by these authors.



photographed from the visible to 750 Å.<sup>44</sup> The Raman spectra of 1,1,1- and 1,1,2-trichloroethane have been compared.<sup>45</sup>

**Physical Constants.** The heat of combustion of gaseous isobutane at constant pressure is  $686.31 \pm 0.13$  Kg.Cal.,<sup>46</sup> and that for tetramethylmethane (neopentane) is estimated as  $840.4 \pm 1.0$  Kg.Cal.<sup>47</sup> The compressibility of gaseous ethane has been determined and an equation of state has been formulated in agreement with the data.<sup>48</sup> The critical constants for propane have been determined.<sup>49</sup> The specific heat data of a number of pure liquid hydrocarbons have been collected.<sup>50</sup> An empirical equation connecting the logarithms of the boiling points and molecular weights has been developed for normal paraffin hydrocarbons (with the exceptions of methane and ethane).<sup>51</sup>

$$\log_{10} T_b (^{\circ} \text{K.}) = 1.07575 + 0.949128 \log_{10} m - 0.101 \log_{10}^2 m.$$

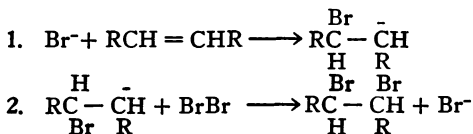
The dipole moments of heptyl bromide and butyl chloride in the vapor state have been determined.<sup>52</sup>

**Patents.** Numerous patents on the replacement of chlorine by fluorine in halogenated organic compounds were granted. The most interesting patent<sup>53</sup> deals with the preparation of  $\text{Cl}_2\text{CF}_2$  from  $\text{CCl}_4$ , HF, and  $\text{SbCl}_5$ . Another fairly large number of patents deals with the preparation of alkyl halides, such as ethyl chloride<sup>54</sup> and *tert*-butyl chloride<sup>55</sup> by conventional chemical methods.

Very little of any theoretical interest is contained in many patents directed toward chlorination, purification, and separation of hydrocarbons, and hence they are omitted.

**Olefins.** A description of the apparatus<sup>56</sup> and the heats of hydrogenation of a few simple olefins has appeared in two papers entitled "Heats of Organic Reactions." The heats of hydrogenation at  $355^{\circ} \text{K.}$  of propylene, butene-1, butene-2 (*trans* and *cis*), and isobutene are 30.115, 30.341, 20.621, 28.570, and 28.289 cal./mole, respectively.<sup>57</sup> Small amounts of oxygen in ethylene-hydrogen mixtures greatly increase initial reaction rates in the homogeneous reaction at  $538^{\circ} \text{C.}$ <sup>58</sup>

The determination of ethylene bonds in the case of simple alkenes can be effected most conveniently by a bromate-bromide titration. In cases of cycloalkadienes the method fails when titrations are made in air.<sup>59</sup> A total asymmetric synthesis by addition of bromine to trinitrostilbene (in a beam of right circularly polarized light of 3600-4500 Å) is claimed.<sup>60</sup> In view of the small rotations observed, duplication of this work by other investigators, and extension in directions suggested by the original investigators, will be awaited with interest. A chain mechanism for the addition of halogens to ethylenic linkages is suggested:<sup>61</sup>



The author extends this view to the addition of halogen acids, in spite of the fact that there is ample literature evidence to the contrary. Nitric acid adds to  $\text{Me}_2\text{-CCHMe}$  and  $\text{iso-C}_4\text{H}_8$  to form the tertiary esters. It does not add to  $\text{C}_2\text{H}_4$ ,  $\text{H}_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$ ,  $1\text{-C}_4\text{H}_8$ , or cyclohexene. The mechanism of the addition is discussed, and the conclusions drawn are applied in the interpretation of the mechanism of nitration in the aromatic series.<sup>62</sup>

Under pressure, ethylene, but not propylene, combines with solid cuprous chloride to give  $\text{CuCl} \cdot \text{C}_2\text{H}_4$ . The dissociation pressure of the compound has been measured at different temperatures.<sup>63</sup>

A study has been made of the effect of radicals in molecules of the type  $\begin{array}{c} | \quad | \\ -\text{C}-\text{C}-\text{COOH} \\ | \quad | \\ \text{Br} \quad \text{Br} \end{array}$  upon treatment with bases. With the proper

choice of substituents, decarboxylation takes place and the bromo olefin (in 70 percent yield) is readily obtained.<sup>64</sup> Reactions of bromo and dibromo olefins with a number of reagents ( $\text{EtOH}$ ,  $\text{EtONa}$ ,  $\text{EtSNa}$ , etc.) are recorded.<sup>65</sup>

An interesting competitive study between ethylene and hydrogen for chlorine has been made. Either in the dark, or when illuminated, ethylene reacts with chlorine preferentially.<sup>65</sup>

The action of oxygen on 2-butene at high temperatures ( $375\text{-}490^\circ$ ) yields mainly acetaldehyde and butadiene, and small amounts of other products.<sup>67</sup> A mechanism involving the intermediate formation of a peroxide is put forward to explain the results. It is of interest in this connection that, when amylene is treated with hydrogen peroxide in the presence of  $\text{FeSO}_4$ ,  $\text{Me}_2\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HCOOH}$ , and  $\text{AcOH}$  are formed.<sup>68</sup>

A large number of unsaturated compounds and unsaturated alcohols were prepared by the condensation of allyl bromide and crotonaldehyde, respectively, with Grignard reagents. These were then converted into alkadienes and alkynes.<sup>69</sup> The formation of tetratriacontadiene by electrolysis of potassium oleate in dilute alcohol has been confirmed.<sup>70</sup> The preparation of crotyl and methylvinylcarbinyl bromides has been reported.<sup>71</sup> The direct addition of organic acids to vinylacetylene yields esters, which polymerize very readily.<sup>72</sup> Further condensations with these esters are described.<sup>73</sup>

The rate of mercuriation of ethylenes has been found to depend on a bimolecular reaction.<sup>74</sup> The effect of surfaces on the addition of bromine to butadiene indicates that, after an initial period, the 1,4-dibromobutane, by forming a unimolecular layer on the glass, becomes the active catalyst.<sup>75</sup>

Boron trifluoride is an effective catalyst in the condensation of propylene and aromatic hydrocarbons. Of interest is the claim that with this catalyst *p*-isopropylbenzene is obtained, while aluminum chloride gives the *m*-derivative.<sup>76</sup> Other investigators claim that at high pressure,  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$  are excellent catalysts for this reaction.<sup>77</sup>

**Patents.** A few interesting patents have appeared. These are briefly mentioned here: the preparation of dichlorobutadiene;<sup>78</sup> oxidation of olefins to oxides;<sup>79</sup> preparation of styrene from ethylbenzene;<sup>80</sup> and the selective halogenation of tertiary olefins.<sup>81</sup>

**Acetylenes.** The following references, already quoted, belong in part to this discussion.<sup>10, 28, 69</sup>

4-Methoxy-2-butyne and 2-octyne react with methyl alcohol in the presence of  $\text{BF}_3$  as a catalyst to give 2,2,4-trimethoxybutane and 3,3-dimethoxyoctane, respectively.<sup>82</sup> Some  $\alpha$ -unsaturated ethers,  $\text{RC(OR') : CH}_2$  are readily obtained by distillation of the 2,2-dimethoxyalkanes with  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ .<sup>83</sup>

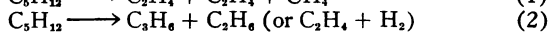
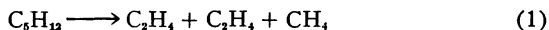
Another paper of the series "Acetylene Polymers and their Derivatives" deals with the polymerization of oxyprenes and their synthesis from vinylacetylene.<sup>84</sup> A physicochemical study of the high-temperature polymerization and hydrogenation of acetylene has appeared.<sup>85</sup>

Some accurate physical constants of dimethylacetylene have been obtained.<sup>86</sup> The dielectric constants of a large number of acetylenic acids (as well as substituted aromatic acids) have been measured in dioxane, and the electric moments computed.<sup>87</sup> The position of the triple bond in acetylenic halides influences the electric moment, which is least with chloro compounds and greatest with iodo compounds. The moments of a large number of acetylenic alcohols have been reported.<sup>88</sup>

**Patents.** It is claimed that organic liquids containing highly reactive acetylenic compounds (or polymers) can be dehydrated with the aid of calcium carbide.<sup>89</sup> The addition of alcohols to mono- and divinylacetylenes presumably takes place when these components are heated in the presence of sodium alcoholate.<sup>90</sup> Mercury sulfonate and benzene-disulfonic acid are supposed to accelerate the addition of acetic acid to acetylene.<sup>91</sup>

**Pyrolysis.** Qualitative experiments on the decomposition of methane, propane, and butane on carbon and platinum filaments indicate that the primary decomposition of methane gives methylene and hydrogen (*cf.*<sup>36</sup>). The energy of activation for the decomposition on carbon is about 95 K. cal./mole.<sup>92</sup> In the case of propane and butane the primary dissociation is into hydrogen and the olefin. Propylene then pyrolyzes into methylene and a lower olefin, while butylene may undergo further dehydrogenation to butadiene.<sup>93</sup> The attempt is made to correlate the pyrolysis of ethane, or rather, the equilibrium constant of the ethane-ethylene-hydrogen equilibrium with the data of the heat of hydrogenation of ethylene; a cause for the discrepancy is suggested.<sup>94</sup>

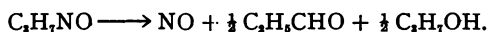
At 600° the thermal decomposition of pentane proceeds according to the following equations:



The effects of external factors on the yields of the different products are discussed.<sup>95</sup> Summaries of data on the pyrolysis of hydrocarbons from the standpoint of thermodynamics and chemical kinetics have appeared.<sup>96, 97</sup>

The thermal decomposition at low pressure of propyl,<sup>98</sup> diethyl,<sup>99</sup> and triethylamines<sup>100</sup> is reported. Intermediate formation of tetra-substituted symmetrical hydrazines is postulated in the case of the last two amines. The hydrazines then undergo further decomposition into nitrogen and hydrocarbons.

In the presence of an inert gas, but not otherwise, ethyl nitrite vapors remove metallic mirrors when passed through a furnace at low pressure.<sup>101</sup> The thermal decomposition of propyl nitrite is formulated as a homogeneous first-order reaction:



It is suggested that the same decomposition takes place in the case of other nitrites. An estimate of the value (strength) of the O-N-bond is made.<sup>102</sup> The initial thermal decomposition of nitromethane into nitrosomethane and oxygen is postulated.<sup>103</sup>

The decomposition of acetaldehyde at equilibrium conditions by different catalysts (Ni proved to be best) into carbon monoxide and methane has been studied. The synthesis from the fragments, however, was not effected.<sup>104</sup>

**Peroxide Effect.** The effect of oxygen in promoting the reaction in an ethylene-hydrogen mixture has already been discussed.<sup>58</sup> In the presence of peroxides hydrogen bromide adds to methylacetylene to give a quantitative yield of 1,2-dibromopropane, while in the presence of antioxidants the 2,2-dibromopropane is formed exclusively.<sup>105</sup> It has been shown that peroxides, and not the solvent, direct the addition of hydrogen bromide to allylacetic acid, and that, in the few cases carefully studied, peroxides apparently have no effect on the direction of addition in molecules which do not contain a terminal double bond, or where the double bond is adjacent to a carboxyl group.<sup>106</sup>

**Polymerization.** The following articles on polymerization have already been discussed.<sup>9, 10, 85</sup>

That unsaturated compounds polymerize under the action of heat and pressure, particularly in the presence of peroxides, has been known for some time. It would appear that the polymerization is a chain reaction, which, in the case of ethylene, is initiated by the presence of free methyl radicals.<sup>107</sup> A well-planned and painstaking attempt at elucidation of the kinetics of ethylene polymerization was unsuccessful.<sup>108</sup>

All of the other work on the polymerization of ethylene, propylene, and butylene deals with conditions<sup>109</sup> and catalysts which produce large quantities of liquid products. The use of phosphoric acid as a catalyst in high-pressure polymerization has given some interesting

results, and some of the resulting compounds have been identified.<sup>110</sup> A review of the work on the polymerization of isoprene has appeared.<sup>111</sup>

The work on polymerization and ring-formation is being continued; the 24th to 27th papers<sup>112a</sup> in the series made their appearance this year. A new class of linear polymers is described  $\dots(\text{CH}_2\text{-O-R-O})_x\dots$ . These were obtained by the action of alkyl formals on glycols above tetramethylene. The behavior of these linear polymers to further polymerization and to depolymerization is described.<sup>112</sup> The other two papers deal with the optimum conditions for depolymerization of linear esters,<sup>113</sup> and the formation of meta and para rings in the condensation of resorcinol and hydroquinone diacetates with glycols of the series  $(\text{CH}_2)_n(\text{OH})_2$ .<sup>114</sup>

4-Cyano-1,3-butadiene has been prepared and found to polymerize to a rubber-like product twenty times faster than isoprene.<sup>115</sup>  $\alpha$ -Dialkylaminomethyl- $\beta$ -vinylacetylenes are prepared from the amine, para-formaldehyde, and  $\text{CH}_2\text{:CHC:CH}$ . When treated with 38 percent HCl containing CuCl, the corresponding  $\alpha$ -dialkylaminomethyl chloroprenes are obtained. These substances polymerize very slowly.<sup>116</sup>

The polymerization of styrene is more sensitive to traces of oxygen than that of heptaldehyde or citral.<sup>117</sup> Mention should be made of a paper on the relation between solvation, solubility and viscosity of polystyrenes.<sup>118</sup>

Heating to a high temperature in an open vessel of cyanamide (free from appreciable amounts of ammonia) gives about 98 percent of the polymerized molecule (dicyanodiamide).<sup>119</sup>

*Patents.* Numerous patents have appeared on the polymerization of the simple olefins by heat and pressure<sup>120</sup> and with catalysts at relatively low temperatures (100-250°).<sup>121</sup> The interest in the polymerization of vinyl compounds to resins has apparently not subsided as yet;<sup>122</sup> the preparation of useful products by polymerization of methylacrylonitrile,<sup>123</sup> ureaformaldehyde,<sup>124</sup> urea, ammonium thiocyanate and urea,<sup>125</sup> of diolefins (butadiene),<sup>126</sup> is claimed. Aldol polymerizes best in the presence of minute amounts of a 30 percent solution of sodium hydroxide. The amount must be so small that the mixture is just alkaline to phenolphthalein.<sup>127</sup>

**Alcohols.** A 14 percent yield of methanol is obtained from carbon monoxide and hydrogen, in the presence of a catalyst (75 atomic percent Zn and 25 atomic percent Cr in the form of their oxides) at 375° and at a pressure of 178 atmospheres.<sup>128</sup> The reduction of aromatic aldehydes by formaldehyde in the presence of alkali leads to excellent yields of some aromatic alcohols (anisyl, piperonyl, and veratryl alcohols).<sup>129</sup> A number of primary alcohols of the type  $\begin{matrix} \text{R} \\ \text{R}' \end{matrix} \text{>CH} \cdot \text{CH}_2 \cdot \text{OH}$  have been synthesized; R and R' are straight chain aliphatic radicals.<sup>130</sup> A large number of high molecular weight  $\alpha,\beta$ -ketoalcohols, up to stearoin, have been prepared.<sup>131</sup> Detailed preparative methods are given for oleyl alcohol (9-octadecene-1-ol),<sup>132</sup> dibutylcarbinol,<sup>133</sup> and trichloroethyl alcohol.<sup>134</sup>

A number of papers dealing with specific analytical tests for alcohols have appeared. It is suggested that methyl alcohol be determined in the presence of large quantities of ethyl alcohol by conversion of the mixture into the alkyl iodides, and combination of the low-boiling fractions with trimethylamine.<sup>135</sup> Isopropyl alcohol is best recognized by oxidation to acetone with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ , and identification of the latter substance.<sup>136</sup> A method has been devised for the analysis of solvents from the butyl-acetonic fermentation of corn mash, containing butanol, acetone, and ethanol in aqueous solution.<sup>137</sup> Some analytical properties of commercial sulfated alcohols useful in the differentiation of these substances from soaps and sulfonated fatty acids are described.<sup>138</sup> A rapid, and what is claimed to be precise, method for the determination of primary and secondary hydroxyl groups in organic compounds, based on the use of acetyl chloride and pyridine, has been reported.<sup>139</sup>

Two papers have appeared on the effect of substituents and of solvents on the reactivity of acyl and alkyl halides with ethyl alcohol.<sup>140</sup> The rate of combination was used as a criterion of reactivity. The solvent was shown to have a significant influence on the rate.<sup>141</sup> It is impossible to summarize these data except to indicate that the differential effects of solvents upon the reactivities of acyl and alkyl chlorides are erratic. Rather disconcerting is the claim that previous observations and calculations regarding the rate of interaction of diphenylchloromethane and alcohol are in error. The data were previously treated upon the assumption that the reaction is reversible; further investigation has yielded no evidence of reversibility.<sup>142</sup>

A study of the vapor pressure-boiling point-composition relations of glycol-water mixtures has shown that they follow Raoult's law rather closely.<sup>143</sup> Large positive deviations from this law were observed, however, in the case of the vapor pressures of binary solutions of ethyl alcohol and cyclohexane.<sup>144</sup> The vapor pressure curves over the range 10-760 mm., the densities, and the indices of refraction have been determined for the following glycols: ethylene, 1,2-propylene, 1,3-propylene, 1,3-butylene, and 2,3-butylene.<sup>145</sup>

An analysis of the x-ray diffraction pattern of methyl alcohol has been made. Of interest to the organic chemist is the suggestion that methyl alcohol shows short-lived hydrogen binding (dipole binding) between oxygen atoms of neighboring molecules.<sup>146</sup>

Within certain limits, *tert*-butyl alcohol was found to be a satisfactory solvent for molecular-weight determinations by the freezing-point method.<sup>146a</sup>

**Aldehydes and Ketones.** The effects of constitution and of reagents on the equilibria of enol-keto tautomers is still attracting a great deal of attention, as evidenced by publications in this country and abroad. The  $\text{HNO}_3$  acid-catalyzed enolization (in the two possible manners) in compounds of the type  $d\text{-C}_2\text{H}_5(\text{CH}_3)\cdot\text{CH}\cdot\text{COR}$ , where R is methyl, ethyl, cyclohexyl or benzyl has been studied in glacial

acetic acid solution. As a check on the method, the rate of racemization of *d*-methylethylacetophenone was compared with the rate of iodination. The two were found to agree very well.<sup>147</sup> The velocity constants of alkaline chlorinations of ketones in solutions more alkaline than 0.3 *M* NaOH, were found to be linear functions of the hydroxyl concentration and the rate of reaction increases in the order: pinacolone, acetone, acetophenone. An interpretation of the results is suggested.<sup>148</sup> A third paper of a series on the Michael condensation deals with the addition of simple ketones to  $\alpha,\beta$ -unsaturated ketones. The data are interpreted upon the basis that an increase in substitution about an active  $\text{CH}_2$  group greatly lowers its reactivity and that the ethyl group is less effective in that respect than the methyl.<sup>149</sup> The acidity of brominated ketones (such as  $\text{MeCOCH}_2\text{Br}$ ) is attributed to the coordination of the CO group with the  $(\text{OH})$  from water. The mechanism of bromination of a number of ketones and aliphatic acids is discussed.<sup>150</sup> It has been shown that the unusual product obtained in the condensation of methylchloroform with phenol in the presence of sodium hydroxide, was not the ketone diphenylacetal or phenyl orthoacetate, but rather the diphenyl ether of ethyleneglycol. As in similar cases, it has been shown that this unusual product arises from an impurity in the starting material—in this case ethylene chloride.<sup>151</sup> Evidence is adduced that the bisulfite addition compounds of formaldehyde are salts of  $\alpha$ -hydroxy sulfonic acids. It is suggested that other aldehyde and keto bisulfites have similar structures.<sup>152</sup>

Pyridine is used as the reagent to displace the equilibrium in oxime formation and thus allow the reaction to proceed to completion. The procedure has been tested for about thirty aldehydes.<sup>153</sup> The effects of hydrogen-ion concentration and of buffer media on the rate of hydrazone formation have been studied. Phosphate buffers were shown to be about ten times as effective as the acetate in catalyzing the formation of phenylhydrazones.<sup>154</sup> The effect of salts on the hydrolysis of diethylacetal, catalyzed by strong acids in water solution, has been studied. From the temperature coefficient of the reaction, the heats of activation were determined and found to be independent of the electrolyte concentration.<sup>155</sup> The rate of diacetone alcohol dealdolization by sodium hydroxide has been studied at various temperatures. Conclusions are drawn with regard to the validity of the collision theory and the entropy of activation for reactions in solution.<sup>156</sup> The condensation of a number of common aldehydes and ketones with nitroaminoguanidine to yield the corresponding nitroguanylhya-zones is reported.<sup>157</sup>

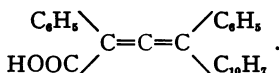
Several papers deal with the physical constants of organic aldehydes and ketones. The ionization potential of acetone vapor was found to be 10.1 volts, in good agreement with that calculated from spectroscopic data.<sup>158</sup> In the far ultraviolet, acetone shows discrete bands above 1300 Å, and only continuous absorption between 1300 and 850 Å. A Rydberg series, converging to an ionization potential of 10.2 volts, was found.<sup>159</sup> The far ultraviolet absorption spectrum of formalde-

hyde has been investigated and a value of 10.83 volts is suggested for the first ionization potential of the C=O bond, and about 164 Cal./mole for the strength of the bond.<sup>160</sup> A very important paper discusses the electron configurations of the normal states for several aldehydes and ketones, and the low excited states of formaldehyde.<sup>161</sup>

**Patents.** The vapor-phase catalytic reactions appear to be the most favored means recorded in the patent literature for the preparation of ketones and aldehydes. Dipropyl ketone is made from butyl alcohol;<sup>162</sup> acetone from ethyl alcohol;<sup>163</sup> glyoxal from acetylene and oxygen in the presence of NO;<sup>164</sup> acetaldehyde from ethyl alcohol and a dehydrogenating catalyst (reduced copper together with 1.5 percent chromium in an inert carrier);<sup>165</sup> and ketones by dehydrogenation of secondary alcohols.<sup>166</sup> The preparation of acetone from acetylene and steam is claimed.<sup>167</sup> Another interesting claim is made, pertaining to the preparation of acetaldehyde and formaldehyde. These substances are presumably formed in substantial amounts when CH<sub>4</sub> and CO<sub>2</sub> are subjected to the action of an electric discharge, the frequency of the A.C. not exceeding 1000 cycles.<sup>168</sup>

Other miscellaneous patents of interest deal with the azeotropic drying of alcohols and ketones;<sup>169</sup> the preparation of ketobutyl derivatives and their uses;<sup>170</sup> separation of isomeric pentanones;<sup>171</sup> concentration of aqueous solutions of formaldehyde,<sup>172</sup> and the preparation of alkoxy acetaldehydes and alkoxyacetic acids.<sup>173</sup>

**Carboxylic Acids.** A most interesting paper deals with the optical resolution of an allenic acid.<sup>174</sup> The resolution was accomplished by means of the brucine salt of its glycolic ester, and rotations of  $[\alpha]_D = +29.5^\circ$  and  $-28.4^\circ$  were obtained for the active glycolic esters of the acids



The effect upon optical rotation of the number of CH<sub>2</sub> groups intervening between the asymmetric carbon atom and a substituent carboxyl group has been investigated in an extensive series of compounds.<sup>174a</sup> The results are correlated in terms of configurational relationships of the acids.

The hydrogenation of carbon dioxide in the presence of a variety of amines yields formic acid or formamides.<sup>175</sup> Acetic acid formation in the vapor phase from methanol and carbon monoxide has been studied.<sup>176</sup> Because of side-reactions, and the short life of the phosphoric acid catalyst, the process is unsatisfactory. Formic acid has been dehydrogenated in the presence of aluminum oxide and phosphate, silica gel, alone, and with phosphorus, thorium, and thallium oxides.<sup>177</sup> Under suitable conditions, at about 300°, 90 percent decomposition occurs.

A method for the preparation of formic acid of high concentration has been described.<sup>178</sup> The statement that *p*-bromophenacyl formate



is a solid derivative of formic acid, melting at  $140^{\circ}$ , is reaffirmed.<sup>179</sup>

It has been reported that the presence of acetic acid permits the direct acidometric titration of *p*-hydroxybenzoic acid, using bromthymol blue as indicator.<sup>180</sup> The hydrogen electrode (Pd and Pt) has been used for the determination of the dissociation constants of a series of acids and amines in ethanol.<sup>181</sup> The relative strengths of a large series of carboxylic and phenolic acids, in butyl alcohol, have been investigated.<sup>182</sup>

The rates of oxidation of formate and oxalate ions by halogens in the dark is in agreement with the empirical expression:  $\text{Rate} = a e^{(nFE/3RT)}$ , where  $e$  is the natural log base,  $E$  is the oxidation reduction potential of the system, and  $n$ ,  $F$ ,  $R$ , and  $T$  are the conventional electrochemical symbols.<sup>183, 184</sup>

Pyruvic acid condenses with veratric aldehyde in alkaline solution to give a 50 percent yield of 3,4-dimethoxybenzalpyruvic acid.<sup>185</sup> Numerous derivatives of this acid are also described.

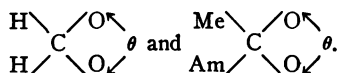
Phenylketene is formed in the dehalogenation of  $\beta$ -bromophenylpyruvic acid by means of aqueous AgOH. Under suitable conditions a 94 percent yield of phenylacetic acid has been obtained.<sup>186</sup> The extension of the method to the preparation of other ketenes is suggested.

The dimensions of the sodium palmitate molecule have been reported<sup>187</sup> to be 23 by 6.2 by 3.7 cm.  $\times 10^{-8}$ .

A method for the determination of thionyl chloride in the presence of its decomposition products was worked out;<sup>188</sup> it is based upon the reactions of thionyl chloride, and its thermal decomposition products, with oxalates and formates.

**Patents.** Catalytic reactions for the preparation of organic acids still hold their preeminence in the patent field.<sup>189</sup> Other patents on acids issued during the year are of little theoretical interest.

**Ethers.** Butan-2-ol is partly polymerized to 3,4-dimethyl-2-hexene, and partly transformed into di-*sec*-butyl ether by 75 percent sulfuric acid at  $80^{\circ}$  under pressure.<sup>190</sup> Variable yields of aliphatic ethers (3-32 percent) are obtained in the interaction of sodium alkoxides with alkyl halides. The bromides are most suitable for this purpose. In addition to ethers, amines and olefins are formed in this reaction.<sup>191</sup> Methods for the preparation of higher 2-alkyl ethers of 1,3-dibromopropane,<sup>192</sup> dialkyl ethers of 2,2-bis-(hydroxyphenyl)-propane,<sup>193</sup> and  $\alpha$ -unsaturated ethers have been described. The  $\alpha$ -unsaturated ethers were made by the distillation of 2,2-dimethoxyalkanes with *p*-toluenesulfonic acid.<sup>194</sup> The electric moments of a number of dialkoxylkanes have been determined.<sup>195</sup> It is claimed that the valence angle ( $\theta$ ) is constant in



Under certain conditions antimony pentafluoride interacts with trichlorodimethyl ether to yield difluorochlorodimethyl ether and trifluoro-

dimethyl ether.<sup>196</sup> The catalytic chlorination of dioxane has been studied.<sup>197</sup>

**Patents.** In spite of the variety of terminology employed (hydration, hydrating, absorption reactions, etc.) it is the old method of preparation of alcohols from olefins in the presence of acid that constitutes the basic idea disclosed in numerous patents granted in this country.<sup>198</sup> The direct oxidation of hydrocarbons to alcohol and alcohols, aldehydes, and acids is claimed in others.<sup>199</sup> New catalysts for the methanol synthesis are claimed.<sup>200</sup> New ethers, particularly mixed tertiary, and improved preparatory methods for known ethers, are claimed.<sup>201</sup> The reviewers have failed to find a "really new idea" in any of the patents. That some of them are definite improvements in the art is not disputed; most of them, however, are "pure invention."

**Esters.** The "acetoacetic ester condensation" has been used to explain the intramolecular condensation of ethyl  $\alpha$ -ethyl- $\alpha'$ -carbethoxyadipate to 2-ethyl-2,5-dicarbethoxycyclopentanone.<sup>202</sup> Two comprehensive papers deal with the mechanisms of reactions of acetoacetic ester, the enolates, and structurally related compounds. In the first paper, carbon and oxygen alkylation is discussed,<sup>203</sup> and in the second the reactions of sodium enolates toward acyl chlorides.<sup>204</sup> The papers do not lend themselves to a brief review, but are strongly recommended to all interested in tautomerism. The cyclization of certain ethylenedimalonic esters by sodium ethoxide to cyclopentanone derivatives has been studied and a reaction mechanism is suggested.<sup>205</sup>

A study has been made of the extent of replacement of one alkyl group by another in the alcoholysis of various acetates. The relative replacing values of fourteen alkyl groups referred to methyl have been calculated.<sup>206</sup> It is claimed that the mechanism of alkaline hydrolysis of ethyl carbonate consists of a reaction of the second order followed by one of the first order. The velocity constants of the two reactions were determined and the temperature coefficients computed.<sup>207</sup>

Methods are given for the preparation of 2,3-dihydroxypropylmalonic ester, its propyl homolog,<sup>208</sup> the glycol esters of dibasic acids<sup>209</sup> (the di- $\beta$ -hydroxyethyl esters), and a synthetic fat (trinonodecylin).<sup>210</sup>

**Patents.** An earnest effort was made by the reviewers to classify the patents on esters, but in spite of many hours of effort the task at the end appeared as hopeless as at the beginning and hence they are omitted.

**Nitrogen Compounds.** The thermal decompositions of amines, nitro compounds, and nitrites have already been discussed.<sup>98-103</sup> The explosion of gaseous diazomethane has been noted at temperatures slightly above those used in measuring the rate of its quiet decomposition. An explanation based upon the Semenoff theory of explosions is advanced.<sup>211</sup> This theory also explains in a reasonably satisfactory way the explosion of ethyl azide.<sup>212</sup>

The dipole moments of nitromethane and chloropicrin were calculated. From a study of the dielectric constant of nitromethane in the

liquid and solid states, the conclusion is drawn that it does not show any molecular rotation in the solid state.<sup>213</sup> The infrared absorption spectra of a number of aliphatic and aromatic nitriles are characterized by a well-defined absorption band at 4.4 for the alkyl and at 4.5 for the aryl nitriles.<sup>214</sup>

Rearrangement of diazo- $\beta,\beta,\beta$ -triphenylethane into triphenylethylene (as the main product) has been effected. A concise discussion of the bearing of these results upon the theory of the mechanism of primary amine nitrite decomposition and some molecular rearrangements is presented.<sup>215</sup> A 26 percent yield of ethylene imine is claimed by the dehydration upon heating of ethanolamine hydrosulfate.<sup>216</sup> The preparation, and some of the properties, of allylnitrosourethane and vinyl-diazomethane have been recorded.<sup>217</sup>

Improved methods have been reported for the preparation of nitroso-methylurea,<sup>218</sup> diazomethane,<sup>219</sup> and acetonecyanohydrin.<sup>220</sup> The series of normal aliphatic thiocyanates has been completed up to fourteen carbon atoms.<sup>221</sup> Four new amidines were prepared by the application of the usual amidine synthesis.<sup>222</sup> The preparation of nitroso-guanidines by reduction of nitroguanidines is of interest. Either catalytic hydrogenation<sup>223</sup> or zinc and ammonium chloride<sup>224</sup> may be employed.

Satisfactory yields of amides containing more than seven carbon atoms are said to result from the interaction of the acids and urea at 180-250°.<sup>225</sup> Several normal fatty acid amides of ethylenediamine have been prepared. The appearance of many under the polarizing microscope is described.<sup>226</sup>

The effect of structure and configuration upon the course of the reaction of acylated ketoximes with alkali has been investigated. Two types of reaction have been found to take place, one a hydrolytic split, and the other a second-order Beckmann cleavage.<sup>227</sup> The reaction of ethyl nitrite with certain isopropyl and cyclohexyl ketones has been investigated.<sup>228</sup> The vesicant properties of chlorinated ethylamines have been pointed out.<sup>229</sup>

*Patents.* Improved methods for preparation of carbonate salts are claimed.<sup>230</sup> Claims are made for the preparation of amines from the alcohols (or phenol) and ammonia with the aid of catalysts in the vapor phase.<sup>231</sup> Glycerol is claimed as a solvent in the condensation of secondary amines with alkyl halides.<sup>232</sup> The successful demethylation of trimethylamine to dimethylamine is claimed.<sup>233</sup> The preparation of amino alcohols is still attracting attention;<sup>234</sup> their preparation by the hydrogenation of monosaccharides in the presence of ammonia and a catalyst is claimed.<sup>235</sup> Numerous amidines have been patented.<sup>236</sup>

**Amino Acids.** An adaptation of the Knoevenagel reaction has led to preparation of some  $\beta$ -amino acids.<sup>237</sup> Note also the preparation of glutamic acid hydrochloride from zein (obtained from gluten press cake).<sup>238</sup> The first of a series of papers on multivalent amino

acids and peptides has appeared. The paper deals with the synthesis of certain quadrivalent amino acids and their derivatives. Conventional methods were employed in the preparation of these substances.<sup>239</sup> The formol titration of amino acids has been studied by two investigators. Both authors reach the conclusion that each amino group reacts with one (or two) moles of formaldehyde, at pH 8-10. The titration constants for arginine, histidine and lysine are given in one paper,<sup>240</sup> and those of glycine, alanine and proline in the other.<sup>241</sup> It has been shown that amino acids are sufficiently basic in glacial acetic acid to permit titration with 0.1 N  $\text{HClO}_4$ .<sup>242</sup>

Several physicochemical papers on amino acids and peptides have appeared. These deal with the compressibility of solutions of amino acids,<sup>243</sup> molal heat capacities,<sup>244</sup> the dielectric constants and electrostrictions of the solvent in solutions of tetrapoles,<sup>245</sup> apparent dissociation constants,<sup>246</sup> heats of solution, heats of dilution and specific heats of aqueous solution,<sup>247</sup> solubilities of derivatives of amino acids in alcohol-water mixtures,<sup>248</sup> and the distribution coefficients of amino acids between water and butyl alcohol.<sup>249</sup> A discussion of any of these papers here is inadvisable in view of the comprehensive and detailed summary of recent physicochemical studies on amino acids and proteins.<sup>250</sup>

**Sulfur Compounds.** A number of alkyl sulfonic acids have been synthesized. The butyl compound was prepared by oxidation of the mercaptan with  $\text{HNO}_3$ .<sup>251</sup> An improvement of the silver nitrate method of determining mercaptans in hydrocarbon solvents has been described.<sup>252</sup>

The reaction of sulfur dioxide and olefins in the presence of peroxides has been carefully studied. Propylene was found to give a polypropylenesulfone. A structure for the compound is suggested.<sup>253</sup> In the third paper of the series the reactions with higher olefins are studied and some limitations of the reaction are indicated. The cleavage of the polysulfones with alkali was carefully studied.<sup>254</sup> Compound formation between a number of aliphatic and aromatic amines and sulfur dioxide is recorded. The 1:1 ratio of  $\text{SO}_2$  to amine predominates in the systems studied, although 1:2 and 2:1 ratios were also obtained.<sup>255</sup> The heats of combustion of 1-cysteine, 1-cystine,  $\beta$ -thiolactic acid and  $\beta$ - $\beta$ -dithiolactic acid are recorded,<sup>256</sup> as well as their heat capacities, entropies, and free energies.<sup>257</sup>

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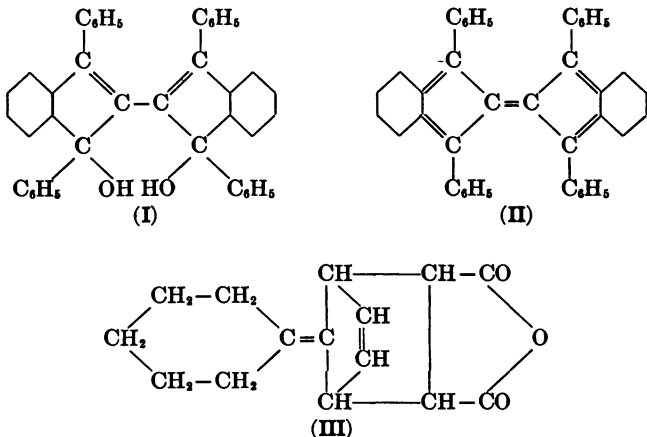
# Chapter XIII.

## Carbocyclic Compounds.

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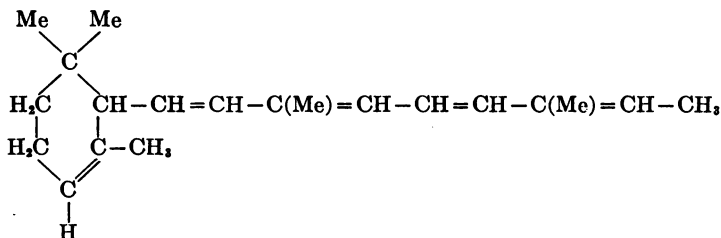
As a result of the interest in carcinogenic, oestrogenic and other biologically active substances, considerable work has appeared on the synthesis of derivatives of phenanthrene and other condensed ring systems, sufficient to justify the inclusion of a section entitled "Polycyclic Compounds." Other fields in which activity continues to be manifested include free radicals, the Grignard reaction, molecular structure, mechanism of reaction and stereoisomerism.

**Alicyclic Compounds.** Bis-2,2'-(1,3-diphenylindenol-3) (I) has been synthesized by Eck and Marvel<sup>1</sup> and by Koelsch and Richter<sup>2</sup> by two different methods; the product proved to be different from that of Dufraisse and Badoche but the difference may be one of stereo-



isomerism. Treatment of the corresponding dichloride with silver did not give the expected rubrene, (II), but 40 percent sodium amalgam appears to give an alkali derivative from which the rubrene may be obtained. The maleic anhydride addition products of all types of fulvenes (III) dissociate in solution at room temperature;<sup>3</sup> the rate of dissociation is greater than the rate of hydrolysis but the addition products may be stabilized by stepwise hydrogenation, the semicyclic double

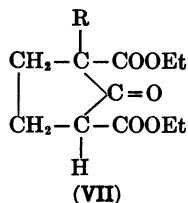
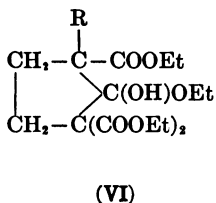
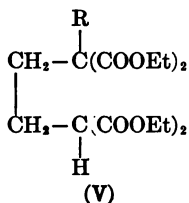
bond being the last attacked. A polyene (probably IV) has been prepared from  $\alpha$ -ionone by Milas and McAlevy which has properties



(IV)

resembling those of vitamin A.<sup>4</sup> Intermediate ketones in the synthesis of perhydrovitamin A have been synthesized by condensing acetylene with  $\beta$ -ionone and with tetrahydroionone using potassium *tert*-amylate as a condensing agent.<sup>5</sup> Some bromine derivatives of indene and indane have been prepared and their structures have been established.<sup>6</sup>

**Compounds Containing Active Methylene Groups.** The action of acetyl and benzoyl chlorides on the sodium derivative of acetoacetic ester gives the *C*-acyl esters directly; the intermediate *O*-acyl derivatives postulated by Claisen are not formed.<sup>7</sup> Further confirmation for the mechanism of the malonic ester condensation proposed by McElvain has been obtained.<sup>8, 9</sup> Esters of the type (V) are cyclized by sodium ethylate through the intermediate aldol (VI) to cyclopentanone derivatives (VII) with elimination of ethyl carbonate. Because of the



absence of an  $\alpha$ -hydrogen in the intermediate, the reaction involving elimination of a molecule of alcohol cannot take place. The condensation of benzoylformanilide,  $\text{C}_6\text{H}_5\text{COCONHC}_6\text{H}_5$ , with malonitrile, cyanoacetamide, ethyl cyanoacetate,<sup>10</sup> acetone, ethyl phenylacetate and diethyl malonate<sup>11</sup> has been investigated. In the Michael condensation of simple ketones with  $\alpha,\beta$ -unsaturated ketones, increase in substitution about an active methylene group greatly lowers its reactivity.<sup>12</sup>  $\alpha,\alpha$ -Dihaloacetophenones containing two ortho groups are acidic, dissolving in alkalis and being regenerated from their salts on acidification.<sup>13</sup>

**Compounds Containing Conjugated Systems.** The addition of Grignard reagents to compounds containing conjugated systems has been the subject of a number of investigations. The properties and

reactions of the ketosulfone,  $C_6H_5COCH=CHSO_2C_6H_5$ , are quite similar to those of dibenzoylethylene;<sup>14</sup> with phenylmagnesium bromide the principle reaction is 1,4 addition to the conjugated system  $C=C-C=O$ , although some 1,2 addition to the carbonyl group takes place.  $\alpha,\beta$ -Unsaturated sulfoxides,  $C_6H_5-CH=CHSOC_7H_7$ , are cleaved by Grignard reagents, a behavior entirely different from that of the sulfones.<sup>15</sup> While ethyl- and phenylmagnesium bromides add 100 percent to the 1,4 positions in benzalpropiophenone, methylmagnesium iodide gives a 75 percent yield of an indene which appears to be derived from a primary 1,2 addition.<sup>16</sup> 2,3-Dimethyl-1,4-naphthoquinone, which reacts more like duroquinone than anthraquinone, gives with phenylmagnesium bromide (a) a reduction product, (b) 1,2 or 1,4 coupling or both.<sup>17</sup> Phenyl- and ethylmagnesium bromides add 1,6 to methyleneanthrone;<sup>18</sup> methylmagnesium iodide and fuchsone give *p*-hydroxy-1,1,1-triphenylethane.<sup>19</sup> These are the only established cases of 1,6 addition of a Grignard reagent to a conjugated system of multiple linkages. Benzalanthrone takes on methyl- or phenylmagnesium bromide in the 1,2 positions, giving a very sensitive dihydroanthranol.<sup>18</sup> Anthraphenone undergoes 1,6 dimolecular reduction with phenylmagnesium bromide but 9,10-dihydroanthraphenone undergoes normal 1,2 addition.<sup>20</sup> These meso-unsaturated anthracene ketones offer striking analogies to  $\alpha,\beta$ -unsaturated ketones. Phenylmagnesium bromide and the ketene,  $Et(EtOOC)C=C=O$ , or its cyclic dimer, give  $\beta$ -keto esters, indicating probably 1,2 addition to the ketene carbonyl group.<sup>21</sup>

Addition of certain mercaptans to the ethylenic linkage of  $\alpha,\beta$ -unsaturated ketones takes place readily without catalysts,<sup>22</sup> thus, benzalacetophenone takes on *p*-tolyl- and benzylmercaptans and forms compounds of the type  $C_6H_5CH(SR)CH_2COC_6H_5$ . Similar addition to corresponding esters takes place if piperidine is present. The mesitylene group has no conspicuous effect on the general reactions of compounds of the type  $C_9H_{11}CH=CHCOC_9H_{11}$ ; corresponding derivatives of triphenylbenzene react less readily but it is difficult to determine to what extent the difference is attributable to space relations.<sup>23</sup> Mesitylbenzylglyoxal  $C_6H_5CH=C(OH)COC_6H_2(CH_3)_3$  is entirely enolic in the solid state but ketonizes to the extent of 10-20 percent in solution; the diortho groups offer steric hindrance to all addition reactions to the carbonyl groups except reduction.<sup>24</sup> Treatment of glycosidic ethers of the type  $C_6H_5C=C(OR)COC(OR)C_6H_5$  with acid or alkali splits

off the glycosidic alkyl group and gives open chain monoalkyl derivatives of benzoylformoin such as  $C_6H_5C(OH)=C(OR)COCOC_6H_5$ .<sup>25</sup> Fuson, Weinstock and Ulliot have found that benzoin can be readily synthesized from  $\alpha$ -ketoaldehydes and aromatic hydrocarbons by the action of aluminum chloride:  $RCOCHO + R'H \rightarrow RCOCH(OH)R'$ .<sup>26</sup> In benzene solution mesitylglyoxal and the corresponding benzoin undergo auto-oxidation and reduction to mesityl phenyl diketone and 1,2-di-(2,4,6-trimethylbenzoyl)-ethylene glycol.  $C_9H_{11}COCH(OH)-$

$C_6H_5 + 2C_9H_{11}COCHO \rightarrow C_9H_{11}COCOC_6H_5 + C_9H_{11}COCH(OH)-CH(OH)COC_9H_{11}$ . Various reactions of compounds containing conjugated systems have been reviewed.<sup>27</sup>

**Free Radicals.** H. Bent and co-workers have been making a careful study of the electron affinity of free radicals;<sup>28-33</sup> all free radicals studied appear to have about the same electron affinity. Dissociation may be explained by assuming that the ethane C-C bond is abnormally weak or that the radicals are stabilized because of a large resonance energy; dissociation appears to be a combination of the two and weakening of the bond may be due to steric hindrance. From results of a quantitative absorption spectra study Anderson has obtained confirmation that triphenylmethyl in ether and sulfur dioxide exists in a quinonoid modification.<sup>34</sup> In dilute solutions in sulfur dioxide there appears to be not only complete dissociation of the ethane but also quantitative formation of the triphenylmethyl cation; in concentrated solutions the color of the free radical may be ascribed to non-ionized triphenylmethyl rather than to the anion.

Marvel and co-workers have synthesized a series of hexa-*p*-alkylphenylethanes<sup>35</sup> and di-*p*-alkylphenyldibiphenyleneethanes;<sup>36</sup> the ethanes are readily oxidized by air to crystalline peroxides; the color of the radicals increases with the weight of the alkyl groups. Free radicals containing the phenanthrene group and the corresponding peroxides have been prepared.<sup>37</sup> Treatment of triphenylchloromethane with silver hyponitrite gives immediate evolution of nitrogen and a variety of products are formed; the intermediate formation of the  $(C_6H_5)_3CO-$  radical is postulated.<sup>38</sup> Triphenylboron adds sodium and is considered to be a free radical.<sup>30</sup> Tri- $\alpha$ -naphthylboron adds two sodium atoms, the second atom being held very much less firmly than the first; conductance experiments reveal, however, that both sodium atoms ionize simultaneously.<sup>33</sup> The two electrons furnished by the two sodium atoms are localized in the ion on a carbon atom in a quinonoid ring.

**Grignard Reaction.** Porter has found that complete racemization takes place in the preparation of the Grignard reagent from an optically active halide.<sup>39</sup> The decomposition voltage of a molar solution of phenylmagnesium bromide is 2.17 volts, which is considerably higher than the decomposition potentials of simple alkylmagnesium bromides.<sup>40</sup> The study of the relative rates of formation of Grignard reagents has been continued; there is no essential difference in the rates of formation of *o*-, *m*-, and *p*-tolylmagnesium bromides, but  $\beta$ -naphthyl bromide reacts less readily than  $\alpha$ -naphthyl bromide, which in turn is less reactive than bromobenzene.<sup>41</sup> Yields of Grignard reagents and organolithium compounds have been compared<sup>42</sup> and the effect of solvent and temperature on the equilibrium:  $2C_6H_5MgBr \rightleftharpoons (C_6H_5)_2Mg + MgBr_2$  has been studied.<sup>43</sup> Directions for the preparation of an effective activated magnesium catalyst are given.<sup>44</sup>

$\alpha$ -Bromoacetomesitylene is largely reduced by magnesium, acetome-

sitylene being obtained in 45 percent yield along with 10 percent of the coupling product, 1,2-di-(2,4,6-trimethylbenzoyl)-ethane.<sup>45</sup> The study of the reaction between Grignard reagents and  $\alpha$ -bromoketones is being continued;<sup>46</sup> the first step probably consists in formation of a complex addition product, which may rearrange into a normal addition product or decompose to give metathetical products, depending upon space relations and relative affinities. The reaction of phenylmagnesium bromide with dibenzylmalonitrile and other malonitriles has been studied; dibenzylmalonitrile adds one equivalent of Grignard reagent to yield a compound which decomposes into phenyl cyanide and  $(C_6H_5CH_2)_2C=C=N MgBr$ .<sup>47</sup>  $\alpha$ -Naphthoic acid can be conveniently prepared from  $\alpha$ -naphthylmagnesium bromide and excess diethyl carbonate, steric hindrance preventing immediate formation of the ketone or carbinol.<sup>48</sup> The Grignard reagent has been applied to the synthesis of anthracene, dihydroanthracene, acenaphthene, fluorene and phenanthrene derivatives.<sup>49</sup> The Grignard reagent does not add to unsaturated linkages of hydrocarbons at temperatures as high as 300°.<sup>50</sup>

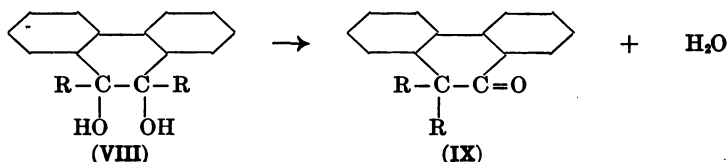
**Methods of Identification.** Aromatic hydrocarbons can be identified by condensing them with phthalic anhydride to *o*-aroylbenzoic acids which can be dehydrated to the corresponding quinones.<sup>51</sup> Aldehydes and ketones can be identified by condensing them with nitroaminoguanidine; hydrolysis with 20 percent hydrochloric acid regenerates the aldehyde or ketone.<sup>52</sup> Phenols can be condensed with 2,4-dinitrochlorobenzene giving highly crystalline stable solids suitable for identification.<sup>53</sup> A number of 3-nitrobenzohydrazones and 2,4-dinitrophenylhydrazones have been prepared for the identification of carbonyl compounds.<sup>54</sup> A large number of aromatic acids have been coupled with benzylamine and  $\alpha$ -phenylethylamine to give derivatives which may serve for identification.<sup>55</sup> Acetyl chloride possesses advantages over acetic anhydride for the quantitative determination of hydroxyl groups; the method is applicable to aromatic alcohols and phenols.<sup>56</sup> Bryant and Smith have discovered that addition of pyridine displaces the equilibrium between aldehyde or ketone and hydroxylamine in the direction of oxime formation, which is an important contribution to the preparation of oximes;<sup>57</sup> by this method, with the modification of leaving out water entirely, the reviewer has prepared oximes which failed to form in aqueous-alcoholic solutions without the addition of pyridine. Contrary to previous reports, *p*-bromophenacyl formate can be prepared.<sup>58</sup>

Quantitative light absorption curves in the infra-red region are given for a number of organic compounds containing the NH, NH<sub>2</sub> and OH groups;<sup>59</sup> it is suggested that these curves should prove suitable for identification of the particular groups and to determine any coupling effects.

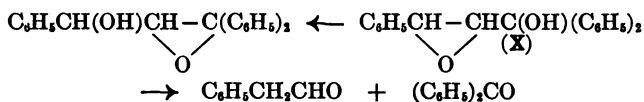
**Molecular Rearrangements.** Stoughton has studied the Fries rearrangement of esters of  $\alpha$ -naphthol and the lower fatty acids; the main product was 2-acyl-1-naphthol in 50-60 percent yields.<sup>60</sup> 4-Acetyl-

1-naphthol gave the same products when treated with aluminum chloride as  $\alpha$ -naphthol acetate; in view of this result it is impossible to state whether the reaction is *intra*- or *intermolecular*. *o*-Isobutylphenol derivatives are conveniently prepared by rearrangement of methylallyl phenol ethers followed by catalytic reduction; furans are also obtained in the rearrangements.<sup>61</sup> Alkenyl ethers of pyrogallol rearrange to alkenylpyrogallols at 200°.<sup>62</sup> Condensation of  $\beta$ -phenylethyl alcohol with phenol gave *p*-( $\alpha$ -phenylethyl)-phenol; dehydration of the alcohol probably precedes addition of the phenol.<sup>63</sup>

Nine diaryldihydrophenanthrenediols (VIII) have been rearranged by Bachmann and Chu; in all cases the group R migrated and diarylphenanthrones (IX) were formed exclusively.<sup>64</sup> According to Kohler

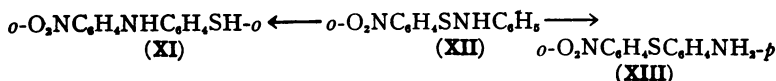


and Bickel  $\beta$ -oxanols of the type (X) may either undergo cleavage or a molecular rearrangement; cleavage depends on replacement of the



hydrogen of the hydroxyl group by a metal.<sup>65</sup> The Grignard reagent from phenyl-*tert*-butyl-*tert*-butylethynylbromomethane gives allene derivatives,  $(\text{CH}_3)_3\text{CC}(\text{X})=\text{C}=\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)_3$ , where X represents the group introduced by the reaction.<sup>66</sup>

A number of rearrangements of nitrogen compounds have been observed. Hellerman and Garner found that diazo- $\beta,\beta$ -triphenylethane  $(\text{C}_6\text{H}_5)_3\text{CCHN}_2$  is readily converted to triphenylethylene by a variety of reagents; acetic and benzoic acids, however, decompose solutions of the diazo compound in a unique way, giving benzyldiphenylmethyl acetate (or benzoate).<sup>67</sup> That the Curtius rearrangement of  $\alpha$ -bromoacid azides can lead to the formation of carbonyl compounds as pointed out by von Braun has been confirmed.<sup>68</sup> *o*-Nitrophenylsulfanilide (XII) was rearranged by heating in the presence of excess of aniline to give a 70 percent yield of *o*-nitrophenyl-*p'*-aminophenyl sulfide (XIII);<sup>69</sup> heating in alcoholic sodium hydroxide solution gave *o*-mercapto-*o'*-nitrodiphenylamine (XI);<sup>70</sup> thus, the sulfanilide may,



depending on conditions, undergo both *ortho* and *para* types of rearrangements.

**Molecular Structure.** Gomberg and Gordon<sup>71</sup> have shown that the colored compounds formed in the reaction between triarylmethylthioglycolic acids,  $R_3CSCH_2COOH$ , and metal halides (or perchloric acid) are not, as has been postulated by Wallis, merely addition compounds of the thio compound with the halochromizing agent, but are double salts of the triarylmethyl halide and the metal halide,  $R_3CCl \cdot MeCl_n$ ; the primary reaction consists in a cleavage of the C-S linkage by the metal halide, forming a triarylmethyl halide, the latter then combining with a molecule of the salt. The color and salt-like character of the compounds are entirely expressed by the quinocarbonium salt structure  $(R_2C=C_6H_4<H)^+X^-$ .

Physical methods have been applied to a considerable extent to determine the structures of compounds. The structure  $(R_2C=OH)^+OSO_3H^-$  is postulated to account for the colors associated with aliphatic and aromatic ketones in sulfuric acid; in xanthone and fluorenone there appears to be stabilization of a quinonoid structure, since new absorption bands are acquired.<sup>72</sup> Piper and Brode<sup>73</sup> have found that, with sufficient separation, the two chromophores in a disazo dye act independently of each other; conjugated or closely linked *para*-coupled dyes show marked deviations from theoretical additive absorption effects. The infra-red absorption spectra of phenylacetonitrile, benzonitrile, and  $\alpha$ -naphthonitrile have been examined.<sup>74</sup> Absorption spectra curves for the sugar phenylosazones confirm the classical formula proposed by Fischer.<sup>75</sup> The general agreement of the mechanical and Raman spectra for benzene is now interpreted as consistent only with the oscillating Kekule formula.<sup>76</sup> The only acceptable structure for naphthalene is the symmetrical Erlenmeyer structure with immobile bonds;<sup>77</sup> this also strongly substantiates the Kekule structure for benzene. The fine structure of naphthacene and condensed quinones has been discussed.<sup>78</sup> From experimental values of the interatomic distances between carbon atoms (C=C, 1.38 Å; benzene, 1.39 Å; graphite, 1.42 Å; C—C, 1.54 Å), Pauling and co-workers<sup>79</sup> have plotted a function showing the dependence of interatomic distances on bond character for single bond-double bond resonance; a small amount of double bond character causes a large decrease in interatomic distance below the single bond value. X-ray investigations support the views that the I-I bond in diphenyliodonium iodide is ionic.<sup>80</sup> Dipole moment measurements indicate that *N*-dimethylantranilic acid exists largely as the "zwitterion," even in benzene solution.<sup>81</sup> Electric moments have been determined for four *p*-substituted phenylethylenes.<sup>82</sup>

The compound, boranilide, reported by Chaudhuri, is probably a double salt of aniline and zinc chloride.<sup>83</sup> The ketene, diphenylacetal, reported by Higinelli, and the phenyl orthoacetate, reported by Heiber, appear to be the diphenyl ether of ethylene glycol.<sup>84</sup>

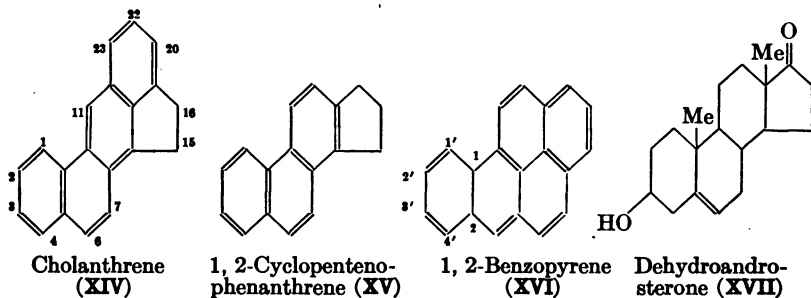


**Organo-Metallic Compounds.** Blicke and Monroe<sup>85</sup> have prepared tetraphenylarsonium bromide,  $(C_6H_5)_4AsBr$ , from triphenylarsine oxide and phenylmagnesium bromide; the corresponding chloride is very soluble in water and the solution is a strong electrolyte. The reactions of phenyl- and diphenylarsine have been further studied.<sup>86</sup> A series of arsenated phenoxyethanols have been prepared by condensing propylene chlorohydrin with 4-hydroxyphenylarsonic acid.<sup>87</sup> Twenty-one different types of mercury derivatives have been synthesized and tested for bacteriological properties.<sup>88</sup> *p*-Cymene was directly mercuroated to give a mixture of monomercurated compounds.<sup>89</sup> The direct mercuration of six polymethylbenzenes has been studied;<sup>90</sup> nitrous anhydride, nitrogen dioxide and nitrosyl chloride give nitroso compounds as primary products with these organomercury derivatives.<sup>91</sup> A carboxylic acid group in the five position has no labilizing effect on the activity of the chlorine atom in 2-chlorophenylarsonic acid;<sup>92</sup> the stibono group is less effective than the arsono group in rendering the halogen labile.<sup>93</sup>

Simons<sup>94</sup> cleaved tetraarylgermanes by hydrogen bromide to triarylgermanium bromide and hydrocarbon; the order of decreasing activity to cleavage is *p*-tolyl, *m*-tolyl, phenyl, benzyl. The electrolysis of sodium triphenylgermanide in liquid ammonia, using a mercury cathode, gave sodium amalgam and varying amounts of hexaphenyldigermane and triphenylgermane.<sup>95</sup>

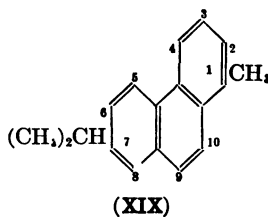
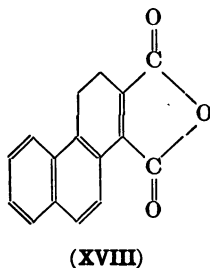
**Oxidation.** Fieser and Fieser are continuing their studies on the oxidation-reduction potentials of  $\alpha$ - and  $\beta$ -naphthoquinones; the effect of substitution is considerably less in the benzenoid nucleus than in the quinonoid nucleus with para quinones; groups which lower the potential of the parent quinone facilitate substitution in the benzene ring and *vice versa*.<sup>96</sup> Substitution of two or more methyl groups in the nucleus of the benzene ring of acetophenone appears to render the nucleus more susceptible to the action of hypohalite solution; unsubstituted derivatives in general are not halogenated, merely undergoing cleavage.<sup>97</sup> Tertiary hydrocarbons of the type  $C_6H_5CH(CH_3)R$ , in which R is methyl, propyl or butyl, on oxidation with gaseous oxygen lose the larger group, acetophenone being formed in each case; as with secondary hydrocarbons, the reaction is not inhibited by water.<sup>98</sup> The oxidation of 5-bromo- and 5-nitropseudocumene has been investigated.<sup>99</sup> Evidence for the existence of semiquinones in the oxidation of hydroquinones has been summarized.<sup>100</sup>

**Polycyclic Compounds.** Fieser and co-workers have been particularly active in the investigation of polycyclic compounds. The carcinogenic hydrocarbon, 20-methylcholanthrene can be obtained in 5.4 percent yield from cholic acid, the most abundant bile acid;<sup>101</sup> the structure of this hydrocarbon, determined by Cook and Haslewood, has been confirmed by synthesis, an isomer also being obtained.<sup>102, 103</sup> Fieser and Seligman have synthesized cholanthrene (XIV), 15;16-benz-dehydrocholanthrene<sup>104</sup> and 16,20-dimethylcholan-



threne;<sup>105</sup> 1',9-methylene-1,2,5,6-dibenzanthracene,<sup>106</sup> 1,2-benzpyrene (XVI), 4'-methyl-1',2'-dihydro-1,2-benzpyrene, 4'-methyl-1,2-benzpyrene<sup>107</sup> and 4'-hydroxy-1,2-benzpyrene<sup>108</sup> have also been prepared. The 2,3-(naphtho-2',3')-acenaphthene of Cook and co-workers has been obtained from 3-*o*-toluoylacenaphthene by the Elbs reaction.<sup>109</sup>

In view of the physiological importance of compounds containing the phenanthrene skeleton, the chemistry of phenanthrene is being intensively investigated. Bachmann<sup>110</sup> has synthesized 1,2-cyclopenteno-phenanthrene (XV) from phenanthrene and has developed a method for synthesizing 1-substituted phenanthrenes. A series of amino alcohols from 1,2,3,4,5,6,7,8-octahydrophenanthrene of the type  $C_{14}H_{17}C(OH)-CH(R)NR'_2$  has been prepared by van de Kamp and Mosettig.<sup>111</sup> Amino alcohols derived from 1,2,3,4-tetrahydrophenanthrene, in which the hydroxyl and amino groups are directly attached to the nucleus, have been synthesized.<sup>112</sup> Phenanthrene derivatives may be prepared by the addition of dienes to maleic anhydride derivatives, followed by decarboxylation and dehydrogenation;<sup>113, 114</sup> thus, from 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride and 2,3-dimethylbutadiene 2,3-dimethylphenanthrene may be obtained. The anhydride of dihydrophenanthrene-*o*-dicarboxylic acid may be readily prepared by the Bougault reaction; condensation of  $\gamma$ -(1-naphthyl)-butyric ester with oxalic ester, followed by treatment with 80 percent sulfuric



acid, yields the anhydride of 3,4-dihydrophenanthrene-1,2-dicarboxylic acid (XVIII); this compound and phenanthrene-1,2-dicarboxylic acid

anhydride possess oestrogenic activity.<sup>115</sup> Dicyclohexenyl-1,1' has been condensed with maleic anhydride and acrolein to give some hydrogenated phenanthrene derivatives.<sup>116</sup> Sulfonation of retene (XIX) gives the 6-sulfonic acid, from which several derivatives were prepared.<sup>117</sup> Phenanthrene and anthracene are preferentially hydrogenated in the 9,10-positions if a copper-chromium-barium oxide catalyst is used.<sup>118</sup> The Grignard reaction has been applied to the synthesis of some *o*-toluoylphenanthrenes;<sup>119</sup> 1-, 2- and 3-benzoylphenanthrenes are obtained through the Friedel and Crafts reaction from phenanthrene and benzoyl chloride;<sup>37</sup> the acetyl group enters the 2-position of dihydrophenanthrene to the extent of 90 percent.<sup>118</sup>

The preparation of glycocholic acid from cholic acid in 40-60 percent yield has been reported.<sup>120</sup> Molecular compounds of desoxycholic acid and certain polycyclic hydrocarbons have been prepared; since the sodium salts of these complexes are soluble in water, this provides a way of obtaining aqueous solutions of carcinogenic compounds.<sup>121</sup> Improvements in the synthesis of androsterone have been made<sup>122</sup> and a method for converting the *cis*-hydroxyl group to the *trans*-form has been developed.<sup>123</sup> The preparation of dehydroandrosterone (XVII) and its oxidation and reduction products have been described.<sup>124, 125</sup> Miller and Bachman<sup>126, 127</sup> have begun a systematic study of fluorene; the structures of several monobromofluorenes, -9-fluorenols and -fluorenones have been established. Sobotka has reviewed the chemistry of the bile acids;<sup>128</sup> Elderfield has done the same for the closely related cardiac glycosides.<sup>129</sup>

**Polymerization.** The polymerization of styrene in the presence and substantial absence of oxygen has been studied; highly purified styrene polymerizes to relatively few large molecules and such a result is explicable if the reaction is catalytic and the catalyst remains attached during the growth.<sup>130</sup> Aromatic mercaptals undergo a condensation reaction with formaldehyde in the presence of acetic and hydrochloric acids to give crystalline products of high molecular weight.<sup>131</sup> 3-Cyclohexylpropene and 3-methylcyclohexene give polysulfones by the addition of sulfur dioxide.<sup>132</sup>

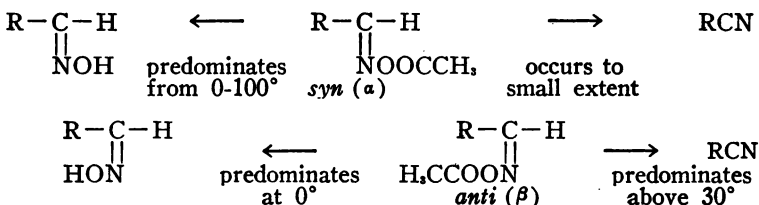
**Pyrolysis.** No significant amount of ketene dimer is produced in the pyrolysis of acetylphthalimide.<sup>133</sup> The C-C bonds which are once removed from the unsaturation rather than adjacent to it undergo pyrolytic rupture; for a type  $C=C-\overset{\alpha}{C}-\overset{\beta}{C}$ ,  $\alpha$  represents strength and  $\beta$  weakness.<sup>134</sup> Instantaneous decomposition of eleven substituted benzalchlorimines has been studied by Hauser, Gillaspie, and LeMaistre;<sup>135</sup> the reaction  $RCH=NCl \rightarrow RCN + HCl$  predominates to the extent of 90 percent at higher temperatures. The thermal decomposition of benzene is a heterogeneous bimolecular reaction, with an apparent activation energy of 50,000 cal.<sup>136</sup> Allyl-*p*-phenetidine decomposes slowly at 270° to give *p*-phenetidine, propylene and resinous products; the initial step appears to be cleavage of the C-N bond.<sup>137</sup>

**Reactions.** For this review the investigations of reactions have been classified roughly according to whether they deal with addition reactions, condensation reactions, mechanism of reaction, rate reactions or reactions not falling into these divisions. Ammonia adds to the double bond of benzylidenemalonic ester to yield  $\beta$ -amino derivatives.<sup>138</sup> Methylamine, ethylamine, and dimethylamine readily add to dibiphenyleneethylene, giving the corresponding alkylaminodibiphenyleneethanes; thus, the properties of the double bond in certain hydrocarbons can approach those of the unsaturated linkage in the grouping  $-\text{CH}=\text{CH}-\text{CO}-$ .<sup>139</sup> Trihalomethyl-*o*- and -*p*-chlorophenylcarbinols are formed by addition of chloroform and bromoform to *o*- and *p*-chlorobenzaldehyde.<sup>140, 141</sup> By addition of hydrazoic acid to  $\alpha$ - and  $\beta$ -naphthoquinones quantitative yields of the 2-amino- and 4-aminonaphthoquinones are obtained.<sup>142</sup> Sulfur dioxide forms loose chemical compounds with aromatic and aliphatic amines.<sup>143</sup> It has been reported that biphenyl forms only a tetraozonide, the non-addition of two more molecules of ozone being attributed to steric hindrance. That this is not the factor involved has been shown in the addition of ozone to 1-phenylcyclohexene-1 and dicyclohexenyl-1,1'.<sup>144</sup>

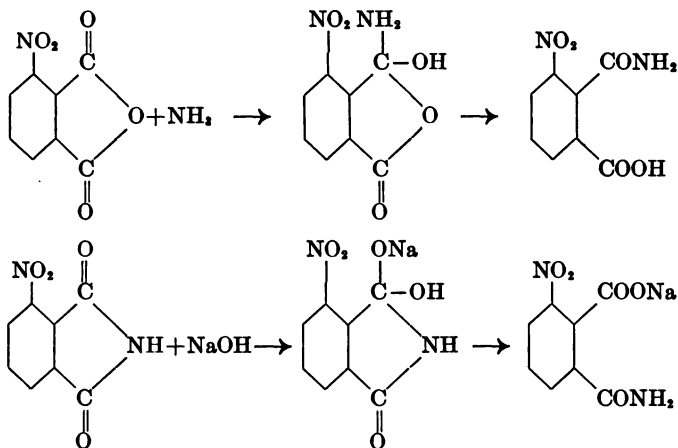
The condensation of propylene with benzene<sup>145</sup> and with *m*- and *p*-hydroxybenzoic acids,<sup>146</sup> and the reaction between naphthenes and olefins in the presence of aluminum chloride and boron fluoride have been investigated.<sup>147</sup> Finely dispersed phosphorus pentoxide is suitable for condensing olefins with aromatic hydrocarbons; benzene and ethylene under pressure gave products from which mono- and hexaethylbenzenes were isolated.<sup>148</sup> Naphthalene gave principally mono- and diethylnaphthalenes. Sodium phenate and amyl bromide can be condensed to amyl phenyl ether in liquid ammonia under pressure.<sup>149</sup> The preparation of chlorobenzophenones by the Friedel and Crafts reaction from benzoic acid and chlorobenzene has been studied.<sup>150</sup> Grosse and Ipatieff have found that paraffins will react with aromatic hydrocarbons in the presence of aluminum chloride; 2,2,4-trimethylpentane and benzene gave isobutane and a mixture of mono- and di-*tert*-butylbenzene.<sup>151</sup> In the Friedel-Crafts reaction between benzoyl chloride and toluene, using mixed catalysts, the formation of a bimetallic complex,  $\text{RCOR}' \cdot \text{AlCl}_3 \cdot \text{FeCl}_3$ , is postulated, since less than one mole of product is formed for each mole of total metal chlorides present.<sup>152</sup> Calloway<sup>153</sup> has prepared an extensive review, with over 500 references, of the Friedel-Crafts reaction.

The mechanisms of a number of reactions have been investigated and in many cases elucidated. Kharasch<sup>154</sup> has reached the conclusion that the Cannizzaro reaction is catalyzed primarily by peroxides; with peroxide-free aldehydes in absence of oxygen no Cannizzaro reaction took place. Michael<sup>155</sup> objects to Wieland's mechanism for the addition of nitric acid as  $\text{HO}-$  and  $-\text{NO}_2$  to a double bond, followed by splitting off of water, and suggests an earlier view that aromatic nitration proceeds in the first phase by aldolization:  $\text{C}_6\text{H}_6 + \text{HONO}_2$

$\rightarrow \text{C}_6\text{H}_5\text{NO}(\text{OH})_2 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$ . From studies made on the rate of hydrolysis of ald-chlorimines to nitriles, evidence has been obtained in support of the mechanism that a proton is removed first, followed by the chlorine ion with a completed electron octet.<sup>156</sup> Both  $\alpha$ - and  $\beta$ -aldoxime acetates undergo fundamentally the same type of



reaction with alkali, forming oximes by hydrolysis and nitrile by elimination of acetic acid.<sup>157</sup> The relative yields of nitriles and oximes formed in the reactions of carbethoxy- $\alpha$ -benzaldoximes are also a function of temperature.<sup>158</sup> Chemical evidence supports the view that, in the formation of amides by the action of ammonia on anhydrides or by hydrolysis of acid imides, the primary reaction is addition to the car-



bonyl group, since different amides are obtained in the two reactions when an unsymmetrical anhydride or imide is employed.<sup>159</sup> The production of sulfides by interaction of sulfur and aromatic amines appears to involve the intermediate formation of a sulfanilide type of compound, followed by rearrangement; the reaction takes place only when a labile hydrogen is present:<sup>160</sup>  $2\text{C}_6\text{H}_5\text{NH}_2 + \text{S} \rightarrow \text{C}_6\text{H}_5\text{NHSHNC}_6\text{H}_5 \rightarrow \text{H}_2\text{NC}_6\text{H}_4\text{SC}_6\text{H}_4\text{NH}_2$ . That the haloform reaction actually involves stepwise halogenation, followed by cleavage, has been demonstrated by Fuson and co-workers<sup>161</sup> through the isolation of the mono-, di- and tribromo derivatives in the bromination of 2,4,6-tribromo-3-acetylben-

zoic acid. Hypiodite reacts with certain hindered methyl ketones to give mono- and diiodomethyl ketones but not triiodo derivatives.<sup>162</sup> The haloform reaction has been reviewed by Fuson and Bull.<sup>163</sup> The mechanism proposed by Lifschitz<sup>164</sup> for the fading of the compound produced by illumination of the leucocyanide of malachite green is inadequate. In the preparation of fuchsine by the formaldehyde process, scission of the diphenylmethane molecule must occur and this supplies only one of the benzene nuclei and the central carbon atom of the triphenylmethane.<sup>165</sup> Further evidence has been obtained that treatment of an unsaturated compound with mercuric acetate in methanol solution results in addition of the intermediate  $\text{CH}_3\text{OHgOOCCH}_3$  to the ethylene linkage.<sup>166</sup> Alkylation of phenols using zinc chloride or boron fluoride is not a direct exchange reaction but is preceded by dehydration of the alcohol and addition of phenol to the unsaturated hydrocarbon.<sup>63, 167</sup>

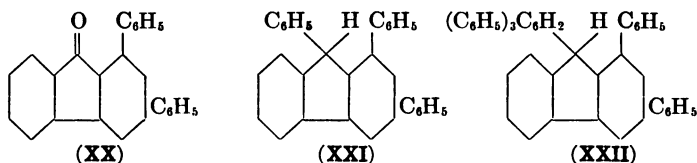
Bachmann<sup>168</sup> has cleaved unsymmetrical ketones by means of potassium hydroxide and measured the relative rates of the two competing reactions:  $\text{R}_2\text{COOH} + \text{R}_1\text{H} \leftarrow \text{R}_1\text{R}_2\text{CO} + \text{KOH} \rightarrow \text{R}_1\text{COOH} + \text{R}_2\text{H}$ ; the resistance to cleavage is a function of the groups. The rates of the chloroform reaction for acetone, acetophenone, and pinacolone have been determined; the increase in reaction velocity with increase in alkalinity is assumed to be due to the ionization of the enolic form.<sup>169</sup> Norris and co-workers<sup>170-173</sup> have been investigating the relative rates of esterification of substituted benzoyl chlorides with alcohols and of etherification of benzyl chlorides; temperature and solvent effects have also been studied. *o*-Aminophenol, cysteine, and potassium sulfite inhibit the absorption of oxygen by alkaline solutions of catechol; pyrogallol and hydroquinone catalyze the oxidation; the reaction probably has a chain mechanism.<sup>174</sup>

The reaction between perthionic acid,  $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$ , and various amines,<sup>175</sup> the properties of 3,4-dimethoxybenzalpyruvic acid and 3,4-dimethoxycinnamic acid,<sup>176</sup> and the reaction between mercury diaryls and diarylselenium dihalides have been the subjects of investigation.<sup>177</sup> Anhydrous zinc chloride catalyzes the pyrolytic decomposition of esters of aromatic acids, giving an unsaturated hydrocarbon and the acid, which in turn may lose carbon dioxide or, if dibasic, form an anhydride.<sup>178</sup> Dehalogenation of  $\beta$ -bromophenylpyruvic acid in aqueous solution gives phenylacetic acid:  $\text{C}_6\text{H}_5\text{CHBrCOCOOH} - \text{HBr} - \text{CO}_2 \rightarrow (\text{C}_6\text{H}_5\text{CH} = \text{C} = \text{O}) + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ; the intermediate formation of phenylketene is postulated.<sup>179</sup>

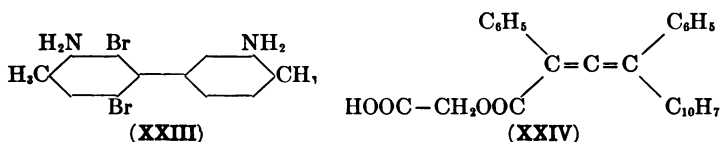
**Reduction.** Lutz and co-workers<sup>180-182</sup> have made a thorough study of the reduction of dibenzoyl ethylene; soluble reducing agents lead to monomolecular products; catalytic reduction and reduction by zinc and acetic acid give open chain and cyclic dimolecular products. It is probable that a conjugate reaction occurs with cyclization taking place through intermediate enolic groups, since the possibility is excluded that the ethylene linkage alone is involved.

Adkins and co-workers have continued their studies on catalytic hydrogenation; the order of increasing resistance to C—O cleavage by hydrogenation is benzyl alkyl ethers, diaryl ethers, aryl alkyl ethers, dialkyl ethers.<sup>183</sup> Reduction of imido ethers in acid solution by sodium amalgam yields aldehydes; electrolytic reduction leads to primary amines.<sup>184</sup> Nitrobenzene undergoes a reduction-chlorination reaction with isopropyl or isobutyl bromide and aluminum chloride, giving a mixture of *o*- and *p*-chloroaniline.<sup>185</sup> The reduction of nitrobenzene with dextrose in alkaline solution has been studied to determine the relative yields of azoxybenzene, azobenzene and aniline under varied conditions.<sup>186</sup> A general method for the catalytic reduction of nitroaryl-arsonic acids to the aminoaryl-arsonic acids has been developed.<sup>187</sup> Hypophosphorus acid is a better reagent than alcohol for converting diazotized amines to hydrocarbons.<sup>188</sup> Treatment of 1,1-diaryl-2-acyl-ethylenes with benzene and aluminum chloride involves both replacement of the aryl groups and hydrogenation:<sup>189</sup>  $\text{Ar}_2\text{C}=\text{CHCOR} + 2\text{C}_6\text{H}_6 + 2\text{H} \rightarrow (\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COR} + 2\text{ArH}$ .

**Ring Closure.** Bogert and co-workers<sup>190</sup> have obtained further evidence that, in the cyclodehydration of aralkyl alcohols, cyclization or polymerization is preceded by olefin formation. Kohler and Blanchard<sup>23</sup> prepared a number of highly phenylated compounds from *sym*-triphenylbenzene; triphenylbenzoic acid,  $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{COOH}$ , is easily condensed to diphenyl fluorenone (XX); triphenylbenzohydrol,  $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{CH}(\text{OH})\text{C}_6\text{H}_5$ , yields 1,3,9-triphenyl fluorene (XXI); and hexaphenylbenzohydrol,  $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{CH}(\text{OH})-\text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3$ , gives 1,3-diphenyl-9-triphenylphenylfluorene (XXII).



**Stereoisomerism.** Adams and co-workers are continuing their investigations of the biphenyl derivatives. A compound (XXIII) with hydrogens in the 2- and 6-positions has been resolved.<sup>191</sup> The ratio of the half-life periods of the optically active 2-nitro-6-carboxy-2'-alkoxy-



biphenyls is  $\text{OCH}_3/\text{OC}_2\text{H}_5/\text{OC}_3\text{H}_7 = 1/5/7$  regardless of the solvent or temperature.<sup>192</sup> Introduction of groups into 2-nitro-6-carboxy-2'-methoxybiphenyl stabilizes it toward racemization in the order nitro > bromo > chloro > methoxy > methyl; this result coincides with the

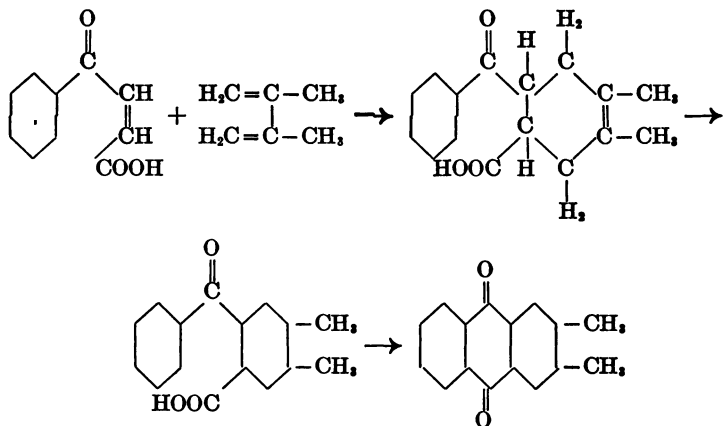
order of increase of the dipole moments of the substituents; the more negative the group the greater is the stabilizing action.<sup>193</sup>

Kohler, Walker and Tishler<sup>194</sup> have resolved an allenic acid (XXIV) into two optically active stereoisomers. Asymmetric syntheses in circularly polarized light have been achieved in the addition of chlorine<sup>195</sup> and bromine<sup>196</sup> to trinitrostilbene; the products lose their activity on standing. Condensation of 2-bromofluorene with *d*-2-octyl nitrate in the presence of potassium ethoxide gave an optically active potassium salt of 9-nitro-2-bromofluorene. Thus a partially asymmetric synthesis has resulted from optically active reagents.<sup>197</sup> The two racemic  $\alpha$ -cyano- $\alpha$ -methyl- $\beta$ -phenylglutaric acids have been resolved.<sup>198</sup> The two methods of preparing 9,10-diaryldihydrophenanthrenediols, (1) by addition of Grignard reagent to phenanthrenequinone and (2) by reduction of 2,2'-diacylbiphenyls, give different pinacols; this difference is probably due to stereoisomerism.<sup>64</sup> The *cis*- and *trans*-2-chlorocyclohexanols have been prepared.<sup>199</sup> The rate of isomerization of *cis*-methyl cinnamate has been studied; a mechanism for the *cis-trans* isomerism, involving excitation of the electrons forming the double bond, is proposed.<sup>200</sup> Acyl derivatives of ketoximes having an hydroxyl, carbonyl, or carboxyl group *alpha* to the C=N linkage undergo hydrolysis if the oximino group is *syn* to the *alpha* standing group and a second order Beckman cleavage (to aldehyde and nitrile) if the oximino group is *anti*.<sup>201</sup> Salts of *d*-camphor-10-sulfonic acid and primary amines exhibit slow mutarotation in anhydrous solvents. This mutarotation is believed due to the establishment of an equilibrium between the *d*-salt and the *l*-anil.<sup>202, 203</sup>

**Substitution and Orientation.** Svrbely and Warner<sup>204</sup> have found that the directing influence of groups appears to be related to the dipole moments; if the moment of a mono-substituted benzene derivative is greater than 2.07D, a second group will be directed *meta*; if less than this value, the entering group will go to the *o*- and *p*-positions. Nitration of *tert*-butylbenzene with mixed acid gives 77 percent *para* and 23 percent *ortho* products.<sup>205</sup> That direct iodination of vanillin gives the 5-iodo derivative has been established.<sup>206</sup> The nitration of polymethylbenzenes has been studied.<sup>207, 208</sup> Sulfonic acid groups on the benzene ring of phenol are stable toward halogenation, even in the presence of acid, if the reaction is carried out in an inert anhydrous solvent.<sup>209</sup> The relative reactivities of the acidic hydrogen in substituted benzoic acids have been compared;<sup>170</sup> for *ortho* groups the order of increased labilizing action is CH<sub>3</sub>O, CH<sub>3</sub>, H, Cl, Br, NO<sub>2</sub>. The dissociation constants of all of the mono- and di-chlorophenols have now been measured in 50 percent methanol solution; the values increase in proportion to the number of substituents and to the proximity of the substituents to the hydroxyl group.<sup>210</sup> Pauling and Wheland<sup>211</sup> have extended the quantum mechanical treatment of Hückel to obtain the charge distribution in aromatic molecules undergoing substitution reactions.



**Syntheses.** Davidson and Bogert<sup>212</sup> have discovered that aromatic alcohols can be prepared from the aldehydes in excellent yields by the "crossed" Cannizzaro reaction, using formaldehyde as the oxygen-acceptor:  $\text{RCHO} + \text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{RCH}_2\text{OH} + \text{HCOOH}$ . The Diels-Alder reaction has been adapted to the synthesis of anthraquinones: aryl-acrylic acids are condensed with butadiene or 2,3-di-

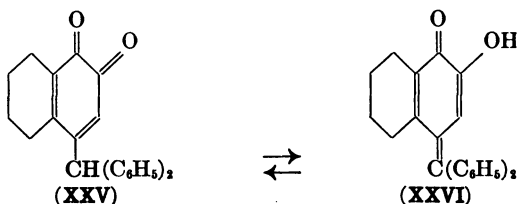


methylbutadiene and the addition product is dehydrogenated and cyclized.<sup>213</sup> The procedure of Staudinger and Freudenberg, employing the action of hydrogen sulfide and hydrogen chloride on the oxo-ketone, has been applied to the synthesis of some new thioketones.<sup>214</sup> The phosphates and alkyl ethers of *o*- and *p*-hydroxybiphenyl<sup>215</sup> and several dialkyl ethers of 2,2-bis-(4-hydroxyphenyl)-propane<sup>216</sup> have been prepared. The optimum conditions for obtaining the best yields of diphenyl sulfide and thianthrene from benzene, sulfur and aluminum chloride have been worked out.<sup>217</sup> Methods for the preparation of chloroacetocatechol,<sup>218</sup> of *m*-chlorofluorobenzene and 2,4,6-trichlorofluorobenzene<sup>219</sup> have been described. Benzotrifluoride and derivatives,<sup>220</sup> some derivatives of *p*-fluorophenylsulfinic acid,<sup>221</sup> and the indium salts of some organic acids have been prepared.<sup>222</sup>  $\omega$ -Mono-, -di-, and -tribenzylacetophenone have been prepared by a sodamide synthesis.<sup>223</sup> Mottern's synthesis of vanillin reported in last year's Survey has been questioned.<sup>224</sup>

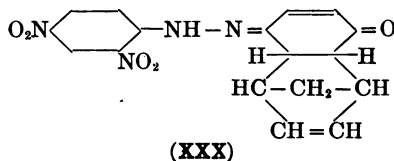
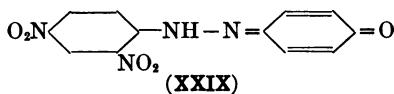
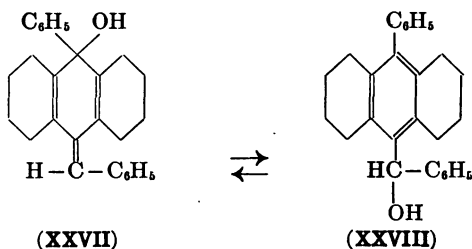
A large number of nitrogen containing compounds have been prepared. Several compounds related to ephedrine have been synthesized.<sup>111, 225, 226</sup> A number of compounds related to novocaine have been prepared; various dye intermediates were coupled with diazotized novocaine<sup>227</sup> and some dialkylaminoethoxyethyl-*p*-aminobenzoates<sup>228</sup> and  $\beta$ -alkoxy-ethyl esters of *p*-aminobenzoic acid were synthesized.<sup>229</sup> Cyclohexylthiocyanate,<sup>230</sup> urethanes derived from phenyl- $\alpha$ -naphthylamine,<sup>231</sup> *p*- and *m*-ethoxybenzylureas,<sup>232</sup> menthyl- and bornylurea,<sup>233</sup>

arylacetic acids and  $\beta$ -arylethylamines from aldehydes,<sup>234</sup> *N*-substituted sulfon-*m*- and *p*-toluidides,<sup>235</sup> *N,N'*-diphenylbenzidine,<sup>236</sup>  $\alpha,\alpha$ -bisbenzoylaminopropionic acid,<sup>237</sup> *N*-acyl-*o*-benzenesulfonaminophenylbenzenesulfonates,<sup>238</sup> acyl derivatives of *o*-anisidine,<sup>239</sup> some new benzene sulfamides and sulfonamides,<sup>240</sup> and some new amidine hydrochlorides<sup>241</sup> have been prepared. Optimum conditions for the practical preparation of *o*-benzenesulfonylaminophenol and *o*-benzenesulfonylaminophenyl benzene sulfonate have been worked out.<sup>242</sup>

Checked directions for the preparation of the following carbocyclic compounds are given in "Organic Syntheses," Vol. XV: 2,6-dibromo-4-nitrophenol, 2,6-dibromoquinone-4-chloroimide, 5,5-dimethyl-1,3-cyclohexanedione, 2,4-dinitroaniline, 3,4-dimethoxyphenylacetic acid, *p*-iodophenol, *o*-nitrophenylsulfur chloride, orthanilic acid, phenylarsonic acid, phenylbenzoyldiazomethane,  $\gamma$ -phenylbutyric acid, phenylglyoxal, 2,4,6-trihydroxyacetophenone,  $\alpha$ -ketotetrahydronaphthalene and 3,4-dimethoxybenzonitrile.<sup>243</sup>



**Tautomerism.** Treatment of 1,2-dihydroxynaphthalene with benzophenone dichloride yields an equilibrium mixture of 4-diphenylmethyl-1,2-naphthoquinone (XXV) and 2-hydroxy-1,4-naphthofuchson (XXVI).



sone (XXVI) instead of the expected diphenylmethylene ether; these fuchsones are quinonoid in structure but not quinone-like in properties other than color.<sup>244</sup> There is some evidence that (XXVII) and (XXVIII) exist in equilibrium in solution.<sup>18</sup> Cyclopentadiene adds to 2,4-dinitrobenzeneazophenol to give the addition product (XXX); it is believed that inner salt formation may stabilize the quinonoid structure (XXIX).<sup>245</sup> The yield of addition product increases with the acidity of the medium. The mesityl group decreases the speed of the enolization,  $>C=C(OH)-R \rightleftharpoons >CH-CO-R$ , to such an extent that the ketone 1,1-diphenyl-2-benzoyl-2-(2,4,6-trimethylbenzoyl)-ethane,  $(C_6H_5)_2CH-CH(COC_6H_5)COC_6H_2(CH_3)_3$ , and its enol exist in stable forms in solution.<sup>246</sup>

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## Chapter XIV.

### Heterocyclic Compounds.

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Perhaps the most interesting development in this field was that dealing with the structure of vitamin B<sub>1</sub> by Williams, Clarke and collaborators. The gross structure of this physiologically important material has apparently been determined and it seems probable that the few remaining uncertain details will soon be solved and a synthesis accomplished. Much of the synthetic work in the field of heterocycles has been stimulated by the aim of preparing products that are either physiologically active or of commercial value. Several very significant contributions have been made on the theoretical side. An attempt has been made by Fieser and Martin<sup>1</sup> to establish the relationship between various kinds of data and the aromaticities of different types of heterocycles. Franklin and Bergstrom<sup>2</sup> have endeavored to correlate the properties of pentacyclic compounds containing one, two, three, and four nitrogen atoms in the ring with those of the well known nitrogen system of compounds and Fuson<sup>3</sup> has offered an explanation of the reactivities of groups located on the  $\alpha$ - and  $\gamma$ -positions of pyridine and related compounds. It is interesting to note that quantum mechanics is even invading the field of organic chemistry; for example, Pauling and Wheland<sup>4</sup> have presented a quantum mechanical discussion of orientation of substituents in some of the more common heterocycles.

**Furans and Oxygen Ring Compounds.** Syntheses of furans from aliphatic compounds have, in general, followed the well known scheme of cyclizing 1,4-diketones in the presence of acid.<sup>5, 6, 7, 8</sup> Zinc bromide has a pronounced catalytic effect in the formation of 2,3,5-triphenylfuran by the zinc-glacial acetic acid reduction of either dibenzoylphenylbromoethylene or dibenzoylphenylethylene.<sup>9</sup> One example of the conversion of a 1-bromo-2-hydroxy-4-keto compound to a furan derivative has been reported.<sup>10</sup> Of interest in the synthesis of furans is the isomerization of methylallylphenols to give the dimethyldihydrobenzofurans; addition of mercuric salts in these reactions produces the mercurated dimethyldihydrobenzofurans.<sup>11</sup>

For the past few years most of the work on the reactions of the furans has been carried out by Gilman and coworkers and has dealt with the fundamental study of orientation. 2-Furfural and isopropyl chloride in the presence of aluminum chloride form 4-isopropyl-2-

furfural, the structure of which was rigorously determined. This is apparently the first instance reported in which substitution occurs in the  $\beta$ -position of a furan when an  $\alpha$ -position is available.<sup>12</sup> This reaction is all the more remarkable, since *n*-, *iso*-, and *tert*-butyl chlorides give with 2-furfural, 5-*tert*-butyl-2-furfural. Another anomalous result was obtained in the study of the alkylation of ethyl 5-bromo-2-furoate, which with the butyl as well as the amyl, hexyl and octadecyl halides gives ethyl 4-*tert*-butyl-5-bromo-2-furoate.<sup>12</sup> The Friedel-Crafts reaction of 2-nitrofuran and propionyl chloride produces 5-chloro-2-furyl ethyl ketone.<sup>13</sup> It has been demonstrated that the pivotally significant "3,5-dibromo-2-furoic acid" of Hill and Sanger is actually 4,5-dibromo-2-furoic acid.<sup>14</sup>

Furan and a number of its derivatives have been oxidized catalytically, giving as the chief solid product maleic acid.<sup>15</sup>

For the first time arsenicals containing the furan nucleus have been prepared. Arsenic trichloride with 2-chloromercurifuran under various conditions gives furyldichloro-, difurylchloro-, and trifurylarsine.<sup>16</sup> On chlorination three separate reactions take place: (1) the oxidation of trivalent arsenic, (2) the saturation of the furan nucleus and (3) the scission of the carbon-arsenic bond. A number of other substituted furan arsenicals were prepared and their behavior towards mercuric chloride studied in order to determine their relative aromaticities.<sup>17</sup>

Tertiary tetrahydrofurylcarbinols are best prepared by the action of the appropriate Grignard reagent upon ethyl tetrahydrofuroate; dehydration of these alcohols takes place readily when they are heated with magnesium sulfate.<sup>18</sup>

Considerable work has been done on dibenzofuran owing, in part at least, to its relationship to morphine. Nitration of dibenzofuran takes place predominantly in the 3-position and, to a limited extent, in the 2-position.<sup>19</sup> However, on dimetalation the 4,6-positions are substituted and, in the 4-methyl and 4-methoxy derivatives, the 6-position is attacked.<sup>20</sup> The relative ease of nuclear substitution reactions of dibenzofuran can be correlated with the hydrogen chloride scission of the 2-, 3-, and 4-dibenzofuryltriphenyl-leads. Pyrolysis of resorcinol over tungstic oxide gives 3- and not 1-hydroxydibenzofuran.<sup>19</sup>

In order to study their physiological action, a number of amino derivatives and amino alcohols of dibenzofuran were prepared.<sup>21, 22</sup> For a similar reason, the benzofuroquinolines were also investigated.<sup>23</sup>

Orientation studies of 1,2,3,4-tetrahydrobenzofurans show that metalation and nitration involve the same relative positions as observed with dibenzofuran and that sulfonation and acetylation take place in the 7-position rather than in the 8-position. Some earlier reported hexahydrodibenzofurans have now been shown to be substituted tetrahydrodibenzofurans, the substituents being in the 7- and not in the 8-position.<sup>24</sup>

2,4,6-Triarylpyrylium acid sulfates are formed from methyl aryl ketones in the presence of sulfuric acid and potassium pyrosulfate.



Curiously, one methyl group is lost in the formation of the pyrylium derivatives from three molecules of the ketone.<sup>25</sup>

The important physico-organic studies on free radicals by Bent and coworkers show that the electron affinities of aryl xanthyl radicals differ little from those of other organic free radicals previously studied.<sup>26, 27</sup> Absorption spectra of xanthone and dibenzodioxin have been determined.<sup>28</sup> Some physical properties of two enantiotropic forms of rotenone have been reported.<sup>29</sup>

Catalytic chlorination of dioxane has been studied and a practical method for the preparation of 2,3-dichlorodioxane developed.<sup>30</sup> This, with a number of Grignard reagents, gives *p*-dioxene. To the unsaturated linkage of *p*-dioxene can be added halogens, hydrogen chloride, and phenylmagnesium bromide.<sup>31</sup>

Further light has been thrown by Spanagel and Carothers<sup>32</sup> on the interesting problem concerning the closure of rings through the *m*- and *p*-positions of the benzene nucleus. Esterification of *m*- and *p*-C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>COOH)<sub>2</sub> with glycols of the series HO(CH<sub>2</sub>)<sub>n</sub>OH, and subsequent depolymerization of the resulting polyesters, yield *m*- and *p*-oxygen-containing rings.

**Sulfur-Containing Rings.** Nitration of bromothiophene yields a bromonitrothiophene, that is believed to be the 2,5-derivative.<sup>33</sup>

Fieser and Kennelly<sup>34</sup> have developed methods for preparing quinones having a thiophene ring in place of the benzene ring of *o*- and *p*-naphthoquinones. Higher reduction potentials of these quinones indicate a lower degree of aromaticity for the thiophene as compared with benzene. Chlorosulfonic acid acts upon retylthioglycollic acid to form 6-retylthioindigodisulfonic acid and the thioindoxyl, ketodihydro-6-retothiophene. The latter readily condenses with aldehydes and is also easily oxidized to the corresponding amorphous thioindigo.<sup>35</sup>

Varying the aluminum chloride content in a semi-quantitative study of the reaction between sulfur and benzene markedly affects the yield of thianthrene.<sup>36</sup>

A cyclic disulfone is formed by the action of normal alkali on polypropylenesulfone<sup>37</sup> and a ring containing two sulfur atoms and six carbon atoms is considered to be formed by the condensation of formaldehyde with *p*-thiocresol.<sup>38</sup>

**Pyrroles, Indoles and Carbazoles.** Quantitative absorption of light in the infra-red region of the spectrum by a number of pyrroles, indoles and carbazoles has been measured by Wulf and Liddel;<sup>39</sup> this absorption is characteristic of the NH group. Ultra-violet absorption spectra for tryptophane and indole have been determined and found to resemble each other.<sup>40</sup>

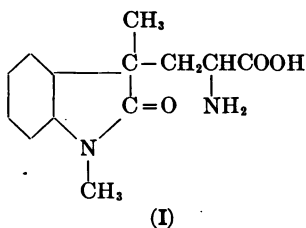
Interesting examples of ring closure yielding pyrrolones and maleinanils have been encountered by Lindwall and coworkers, when condensation products of benzoylformanilide with such compounds as acetophenone,<sup>41</sup> diethyl malonate<sup>42</sup> and ethyl cyanoacetate<sup>43</sup> are treated with acid. The equilibrium between proline and formaldehyde

has been studied<sup>44</sup> and potentiometric titration curves for proline and tryptophane have been described.<sup>45</sup>

A new method for the preparation of porphyrins, which consists of interacting pyrrole and aldehydes, has been described by Rothmund. The reaction between formaldehyde and pyrrole is believed to give porphin, the parent ring system of the porphyrins.<sup>46</sup> Pyrroporphyrin, a chlorophyll decomposition product, has been isolated from beef bile; spectroscopic examination indicates that traces of coproporphyrin are also present.<sup>47</sup> Absorption spectra of oxidized and reduced hemin and hemochromogens have been described<sup>48</sup> and the relative rates of absorption of carbon monoxide by reduced hemin and pyridine hemochromogen have been determined.<sup>49</sup>

Diazoesters act upon indole to give 3-substituted as well as a small amount of 1,3-disubstituted derivatives. Jackson and Manske<sup>50</sup> have found this reaction to be a convenient one for the synthesis of a wide diversity of indole compounds and have utilized it to develop a practical synthesis of indolyl-3-acetic acid.

The fundamental studies of Julian and coworkers in the indole series have been directed towards the syntheses of physostigmine<sup>51, 52, 53</sup> (see Chapter XV on "Alkaloids") and oxytryptophane, which is considered to be the first product formed in the intermediary metabolism of tryptophane. Although the latter goal has not yet been attained, they have succeeded in preparing the closely related dimethyl derivative (I) by



the following series of reactions. 1,3-Dimethyloxindole was condensed with bromoacetal, the product hydrolyzed and the aldehyde converted by means of the Strecker synthesis into the amino acid. Attempts to carry out the same reaction with oxindole failed, because of difficulties met with in the initial condensation with bromoacetal. A number of other possible routes for the synthesis of oxytryptophane were explored.<sup>54</sup> Also, of considerable significance in the study of the metabolism of tryptophane is the work of Gordon and Jackson.<sup>55</sup> They prepared amino-*N*-methyl-, Bz-3-methyl-, and Pr-2-methyl-tryptophane and found that only the first is capable of stimulating growth in rats subsisting on a diet deficient in tryptophane. This is suggestive that the *N*-methyl amino acids may be metabolized and utilized in place of the natural amino acids.

$\beta$ -Naphthisatin<sup>56</sup> has been combined with acetophenone, acetone, and nitromethane in order to correlate its condensation reactions with those

of isatin.<sup>57</sup> Aldols were obtained that dissociate in solution when heated and that suffer dehydration when subjected to acid.

Improvements in the Fries-Rosenmund rearrangement of *N*-acetyl to 3-acetylcarbazole have been made; 1-acetylcarbazole is a by-product in this reaction.<sup>58</sup>

**Pyridines and Quinolines.** Byrant and Smith have utilized pyridine (1) to displace the oxime synthesis equilibrium in the direction of completion (for the determination of aldehydes and ketones),<sup>59</sup> (2) for the rapid determination of primary and secondary hydroxyl groups by means of acetyl chloride<sup>60</sup> and (3) for the determination of water in organic liquids.<sup>61</sup>

Pyridyl and quinolyl acrylic acid dibromides have been prepared by Alberts and Bachman<sup>62</sup> and their dehalogenation with bases studied. Rather curiously the original acrylic acids were found to be the principal products of the reaction. Pyridylchloroethylene with alkali gives  $\beta$ -pyridylacetylene. The malonic ester grouping has been introduced in the 2-position of pyridine with the aim of using it as an intermediate for the preparation of pyridyl substituted barbituric acids.<sup>63</sup> Volume XV of "Organic Syntheses" contains directions for the preparation of 1-methyl-2-pyridone.<sup>64</sup>

The interesting rearrangement of indoles into quinolines has received additional study; condensation products of isatin and malonic acid derivatives<sup>65</sup> and of  $\beta$ -naphthisatin and ketones<sup>66</sup> on acid treatment give quinolones. The oxido-reduction systems from quinoline- and isoquinoline-5,8-hydroquinone have been studied potentiometrically.<sup>1</sup> 5-Benzyl-8-hydroxyquinoline has been prepared by a modified Skraup's reaction for bactericidal tests<sup>67</sup> and improvements have been made in the Skraup synthesis of *o*-phenanthroline, the ferrous complex of which is an excellent oxidation-reduction indicator.<sup>68</sup> 1-(2-Quinolyl)-4-allyl thiosemicarbazide is a sensitive precipitant for cadmium ion.<sup>69</sup>

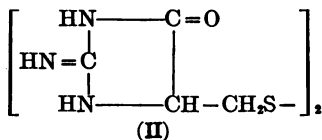
Bromination of a number of aminovaleric acid derivatives results in ring closure to give dibrominated  $\alpha$ -piperidone derivatives.<sup>70</sup>

The equilibrium between pyridine, hydrogen, and piperidine has been measured and the heat of reaction and accompanying free energy change calculated.<sup>71</sup> Catalytic hydrogenation of several nicotinyl acyl methanes results in the formation of a variety of products in which the pyridine ring is reduced and the 1,3-diketone moiety hydrogenolyzed.<sup>72</sup> Reduction of carbon dioxide in the presence of piperidine gives *N*-formylpiperidine.<sup>73</sup> The relative reactivities of nine different 2- and 2,6-disubstituted piperidines towards butyl bromide have been determined.<sup>74</sup> Several piperidine and isoquinoline derivatives of tetrahydrophenanthrene have been synthesized.<sup>75</sup>

**Imidazoles, Pyrimidines and Purines.** Much of the synthetic work carried out in this group has been motivated by the possibility that the compounds prepared might possess pharmacological activity. Higher members of the alkyl glyoxalidines have been prepared by an improved

Hofmann synthesis.<sup>76</sup>  $\beta$ -Diethylaminoethoxy derivatives of several pyrimidines (and quinazoline) were synthesized by treating the sodium salt of the amino alcohol with the chloropyrimidines.<sup>77</sup> Many 5,5'-disubstituted barbituric acids have been prepared by an improved procedure.<sup>78</sup> New types of barbituric acids contain  $\beta$ -picolyl<sup>79</sup> and acetanilido<sup>80</sup> groups in the 5-position. Of theoretical interest is the preparation of 5,5'-diphenylbarbituric acid by condensing benzene and alloxan in sulfuric acid.<sup>81</sup> Some thiobarbituric acids have been found to be powerful hypnotics.<sup>82</sup>

A new practical synthesis of carnosine,  $\beta$ -alanyl-*l*-histidine, has been developed by Sifferd and du Vigneaud.<sup>83</sup> Carbobenzoxy- $\beta$ -alanine is converted to the acid azide which is condensed with the methyl ester of *l*-histidine to give carbobenzoxy-carnosine. Saponification and removal of the carbobenzoxy group by catalytic hydrogenation resulted in the formation of carnosine. Cystine cyamidene (II) has been prepared from  $\alpha$ ,  $\alpha'$ -diguanido-di-( $\beta$ -thiopropionic acid) and, like analogous disulfides, is very labile in alkali.<sup>84</sup>



Addition products obtained from aromatic amidines and glyoxal, when treated with an aromatic aldehyde and alkali, give compounds that are considered to be diphenylhydroxypyrimidines (or benzoyl-phenylglyoxalines).<sup>85</sup>

Cytosine has been synthesized by the ammonolysis of 1,2-dihydro-2-keto-4-ethoxypyrimidine, which is obtained by the alkaline treatment of 2,4-diethoxypyrimidine.<sup>86</sup> Various substituted ethylmercaptopyrimidines, when treated with chlorine in water, are converted to the sulfones; these on acid hydrolysis yield the corresponding oxypyrimidines.<sup>87</sup>

Of considerable importance is the recent work of Levene and Tipson. Trityl and tosyl derivatives of thymidine have been prepared and from their behavior it has been deduced that the sugar is a furanoside. This information offers an explanation for the differences in the behavior of the ribo- and desoxyribonucleic acids. Structures have been assigned to these acids which are in agreement with the facts.<sup>88</sup> In the partial synthesis of nucleotides, inosine is converted to the monoacetone inosine, which, on phosphorylation and subsequent hydrolysis, yields hypoxanthine-5-phosphoribofuranoside, which is claimed to be identical with muscle inosinic acid.<sup>89</sup>

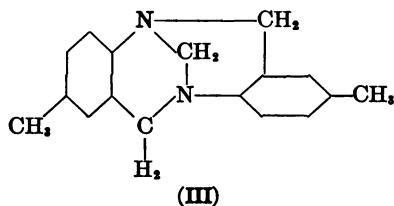
A new method for the estimation of purines in tissues has been proposed<sup>90</sup> and improvements in the micromethods for the determination of uric acid, creatinine, and allantoin have been described.<sup>91</sup>

Some properties of hepatoflavin<sup>92</sup> and of imidazole flavianates<sup>93</sup> have been studied and the titration constants of a number of imidazoles

have been determined.<sup>94</sup> A systematic study of the equilibria between formaldehyde and histidine or histamine has been developed.<sup>95</sup> Heats of combustion,<sup>96</sup> heat capacities and entropies<sup>97</sup> of naturally occurring purines have been reported. Of considerable practical importance is the description of the preparation of the pure purines.

**Quinazolines, Piperazines and other Nitrogen Ring Systems.** In order to study their physiological effects, quinazoline derivatives have been synthesized<sup>98</sup> that are structurally related to some of the angostura alkaloids. 2-Veratryl-6,7-dimethoxyquinazoline, which is structurally related to papaverine, has also been prepared.<sup>99</sup> This work also includes some fundamental information on the chemistry of quinazoline. 2,4-Dichloroquinazoline behaves like a typical imino-chloride and reacts with ammonia or methylamine to give the corresponding diamino-quinazolines.<sup>100</sup>

On the basis of acylation, nitrosation and reduction studies and of a new synthesis, Spielman<sup>101</sup> has assigned to Tröger's base, which is prepared from *p*-toluidine and formaldehyde, the tetrahydroquinazoline



structure (III). Subsequently Wagner<sup>102</sup> determined the probable mechanism involved in its formation.

*N,N'*-Disubstituted piperazines are obtained by condensing piperazine or *N*-phenylpiperazine with derivatives of monochloroacetic acid,<sup>103, 104</sup> with ethylene oxide<sup>105</sup> (for the preparation of procaine analogs), and with aldehydes, in the presence<sup>106</sup> or absence<sup>107</sup> of reducing agents. Piperazine adds to the ethylenic linkage of maleic or fumaric esters to give piperazino-1,4-bis-(alkyl succinates).<sup>108</sup>

In very dilute solution  $\gamma$ -bromopropyltrimethylamine reacts intramolecularly to form the cyclic dimethyltrimethyleammonium bromide, which rearranges slowly to give a linear polymer. The impure diethyl analog behaves similarly, although rearranging less readily. Under the same conditions cyclic salts with alkyl groups higher than ethyl do not change into polymeric products.<sup>109</sup>

A quinoxaline derivative<sup>110</sup> was formed by the condensation of a monomethyl ether of benzoylformoin with *o*-phenylenediamine and a pyrazoline derivative<sup>111</sup> by the action of diazomethane on a 1,4-naphthoquinone.

Methods have been investigated and developed for preparing *lin*-bis-triazoloquinone and quinones of the benzo-<sup>112</sup> and naphthotriazole series.<sup>113</sup> Some of these products were studied potentiometrically and

the bearing of the results on the fine structure of the triazole ring discussed.

An interpretation of the reversible oxidation-reduction exhibited by certain phenazines has been presented,<sup>114</sup> and the mechanism of the chemiluminescence of 3-aminophthalhydrazide investigated.<sup>115</sup>

**Miscellaneous Nitrogen, Oxygen, and Sulfur-Containing Rings.** Certain carbocyanine dyes containing the chain  $=\text{CHC}(\text{CH}_3)=\text{CH}-$  can now be prepared by the new method of heating, in a basic medium, a quaternary salt of a heterocyclic ammonium base containing a reactive methyl group.<sup>116</sup> Improvements have been made in the old methods for making these dyes<sup>117</sup> and the 2'-cyanines,<sup>118</sup> and many new types containing the oxazole, thiazole, selenazole and pyridine rings were synthesized. Optical and photographic properties of many of these new dyes are recorded.<sup>119</sup>

Phenylated benzoxazoles<sup>120</sup> were prepared from *o*- and *p*-hydroxydiphenyls and converted into azo dyes. These dyes were examined spectroscopically and a study made of their tinctorial properties.<sup>121</sup> Nitrostilbenes or their components are converted by alcoholic ammonia into isoxazoline oxides, which are considered to be intermediates in the formation of triphenylisoxazol derivatives by the Knoevenagel reaction.<sup>122</sup> *N*-Acyl-2-aminoethanols yield  $\Delta^2$ -oxazolines under conditions favoring dehydration and  $\Delta^2$ -thiazolines when heated with phosphorus pentasulfide.<sup>123</sup>

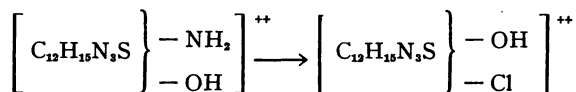
Anils are intermediate products in the formation of benzothiazoles from either *o*-aminothiophenol, its zinc salt or the disulfide.<sup>124</sup> Condensation products of the indirubin type are obtained by the interaction of 2-methylbenzothiazoles with isatin or certain of its derivatives. Isatin  $\alpha$ -chlorides give either  $\alpha$ - or  $\beta$ -condensations, depending upon the experimental conditions. As dyes, these products proved to be of little value.<sup>125</sup> Fluorinated thiazoles<sup>126</sup> and aryl substituted thiazolidones<sup>127</sup> have been synthesized. Alkylation of any of the latter produces two isomeric products, the structures of which were determined.

Dithiazanes are formed when methylene dihalides react with thiourea, monoarylthioureas and 1,5-diaryldithiobiurets.<sup>128</sup> Perthiocyanic acid reacts with a number of *o*-substituted aromatic amines to give fused side rings.<sup>129</sup> A practical method for the preparation of rhodamine has been reported.<sup>130</sup>

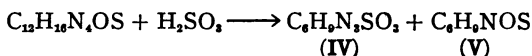
Sultams of the camphor series are prepared by dehydration of certain *N*-phenylaminocamphanesulfonic acids.<sup>131</sup>

**Vitamin B<sub>1</sub>.** Intense activity and competition and considerable progress have marked the study of the structure of vitamin B<sub>1</sub> by the group of collaborators, namely, Williams, Clarke, Buchman, Wintersteiner, Gurin, Ruehle, Waterman, and Keresztesy at Columbia University. Analyses of the purified crystalline hydrochloride, which has been made available in comparatively large amounts<sup>132</sup> agree best, when calculated as the base, with the formula  $\text{C}_{12}\text{H}_{16}\text{N}_4\text{OS}$ ,<sup>133</sup> in agreement with the formula adopted earlier by Windaus, Tschesche,

and Ruhkopf.<sup>134</sup> The absorption of vitamin B<sub>1</sub> in the ultra-violet region of the spectrum, has been described by a number of groups of workers but the results differed, usually in detail. Ultra-violet absorption of the purified hydrochloride in either aqueous or alcoholic solution is now reported<sup>135</sup> to occur as two bands, one at 235μ and the other at 267μ. Evidence for the presence of an amino and an aliphatic hydroxyl group is obtained by heating the vitamin with hydrochloric acid; the amino group is hydrolyzed and the —OH is replaced by non-ionic chlorine.<sup>135</sup>

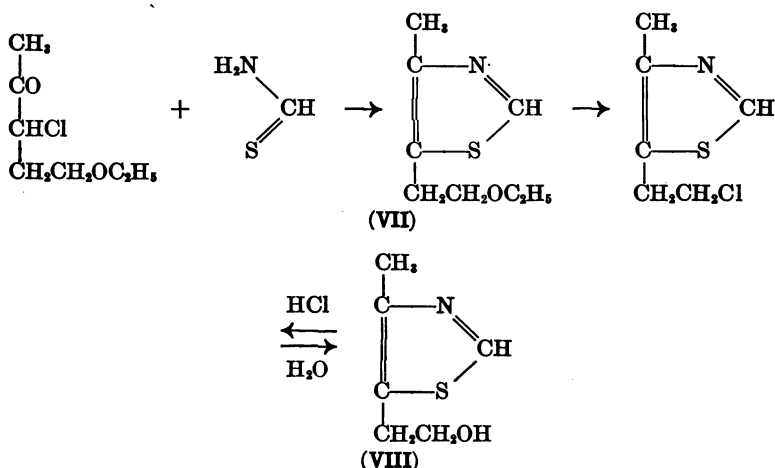


In the degradative studies ingenious use was made of the observation that sulfurous acid as a preservative against bacterial decay of rice polish extracts resulted in a rapid loss of their antineuritic activity. Careful examination of this curious reaction yielded fruitful results. When vitamin B<sub>1</sub> is subjected to the action of sulfurous acid at pH 5 a rapid scission into two fragments, one acidic (IV) and the other basic (V) is effected.<sup>136</sup> The basic product (V), which is an oil, was

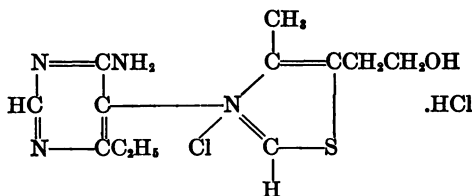


converted into a number of crystalline salts and on treatment with *p*-nitrobenzoyl chloride yields a *p*-nitrobenzoate, which still exhibits basic properties. This is considered to be evidence for the presence of an —OH group and of a tertiary nitrogen atom in (V). Additional evidence in favor of this view was secured by converting (V) into an organic chloro compound by heating with hydrochloric acid [ $\text{C}_6\text{H}_9\text{NSO} \rightarrow \text{C}_6\text{H}_8\text{NSCl}$  (VII)] and into a methiodide, which, with alkali, does not regenerate an ether soluble base. Oxidation of (V) with nitric acid gives a sulfur-containing acid (VI) [ $(\text{C}_4\text{H}_4\text{NS})\text{-C}_2\text{H}_4\text{OH} \rightarrow (\text{C}_4\text{H}_4\text{NS})\text{-COOH}$  (VI)], which proved to be identical with the acid obtained by Windaus, *et al.*,<sup>137</sup> by direct nitric acid oxidation of vitamin B<sub>1</sub>. From a consideration of this information, together with the optical inactivity of (V) and the absence of iodoform when subjected to alkali and iodine, it was inferred that (V) is a tertiary heterocyclic base with a β-hydroxyethyl side chain.<sup>138</sup> The behavior of the vitamin and the basic cleavage product (V) toward alkali plumbite, toward bromine and toward nitric acid suggests that they are derivatives of thiazole;<sup>139</sup> absorption spectra also support this deduction.<sup>140</sup> The nitric acid product (VI), therefore, was expected to be a thiazole-carboxylic acid, and work in the characterization of this was facilitated, as its properties agreed closely with those of the known 4-methylthiazole-5-carboxylic acid. Comparison of the methyl ester of this thiazole with the methyl ester of (VI) showed them to be identical.<sup>139</sup> Tomlinson

has also reported that the synthetic thiazolecarboxylic acid is identical with (VI).<sup>141</sup> In view of this result the basic cleavage product (V) of the vitamin was expected to be 4-methyl-5- $\beta$ -hydroxyethylthiazole (VIII), and this was rigorously established by the syntheses of (VII) and (VIII) and the comparison of their properties with those obtained from the natural products.<sup>139</sup>



Although there can be no question as to the structure of the thiazole portion of the vitamin, there remains some doubt as to the constitution of the other fragment. In addition to the thiazole, sulfite treatment of the vitamin gives a practically quantitative yield of a crystalline "amino sulfonic acid" (IV) and this on hydrolysis with concentrated hydrochloric acid liberates ammonia and gives an "oxysulfonic acid." Since the chemical characteristics are similar to those of cyclic amidines and the absorption spectra in particular resemble those of 4-aminopyrimidines (in contrast to those of 2-aminopyrimidines) (IV) is considered to be a 4-aminopyrimidine.<sup>143</sup> The following tentative structure for vitamin B<sub>1</sub> hydrochloride which is consistent with all of the above data has been proposed by Williams.<sup>144</sup> Inspection of this formula



shows the presence of quaternary nitrogen and evidence in favor of this has been obtained by titrative<sup>145</sup> as well as by comparative chemical studies.<sup>139</sup> However, evidence in regard to the presence of



an ethyl group (or two methyls) or the position to which it and the thiazole group are attached is lacking. Windaus, *et al.*<sup>146</sup> favor a structure which differs from that of Williams only by having methyl groups attached to the (2) and (6) positions in place of the ethyl group in the (6) position, since they believe such a structure accounts more easily for the formation of a nitric acid oxidation product,  $C_7H_{11}N_3O_5$  (ethyl ester), which has not yet been characterized.

Attempts to synthesize the "pyrimidine" portion of vitamin  $B_1$  have also been made. Robinson and Tomlinson<sup>147</sup> and Buchman<sup>142</sup> independently have synthesized 4,5-diamino-6-ethylpyrimidine. Johnson and Litzinger<sup>148</sup> have described some of the properties of uracil-5-methylamine, which they believe will be of interest in the development of the chemistry of vitamin  $B_1$ .

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## Chapter XV.

### Alkaloids.

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There has been in recent years a marked and gratifying development of interest in the field of natural products among American chemists. This is reflected in the increasing number of publications dealing with the isolation, structure, and synthesis of alkaloids, and with the relationship between structure and physiological action. The present review covers advances in the chemistry of the plant alkaloids in the period 1933-1935, with additional references to such pharmacological studies as are pertinent to the alkaloid groups discussed.

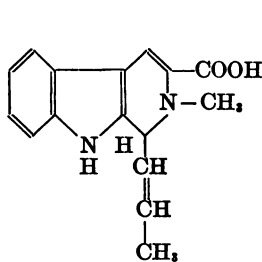
**Ergot Alkaloids.** The discovery of a new ergot alkaloid of exceptionally high oxytocic power is undoubtedly one of the outstanding recent contributions of chemistry to medicine, and it is regrettable that the issue of priority has become so prominent. The observation of Chassar Moir<sup>1</sup> in 1932 that the water-soluble fraction of certain ergots possessed unexpected physiological action on oral administration appears to have furnished the stimulus<sup>2</sup> that has led to the isolation of the crystalline base,  $C_{19}H_{23}O_2N_3$ , known (in alphabetical order) as ergobasine,<sup>3, 4</sup> ergometrine,<sup>5, 6, 7</sup> ergostetrine or x-alkaloid,<sup>8-13</sup> and ergotocin,  $C_{21}H_{27}O_3N_3$ .<sup>14-19</sup> The descriptions of the alkaloid published by the several investigators agree remarkably well, and the consensus of opinion is that the four above-named bases are identical.<sup>2, 4, 6, 7, 12, 20</sup> The physical properties (melting point, optical rotatory power) of the new alkaloid appear to be changed by intensive purification<sup>12</sup> or by prolonged standing of the base in methanol solution, but the change, if a structural one, does not greatly affect the physiological action.<sup>21</sup> In contrast to most other ergot alkaloids, the base yields no ammonia on alkaline hydrolysis. The fragments isolated are lysergic acid, and a dextrorotatory aminopropanol, thought to be derived from *d*-alanine, whence it appears that the new alkaloid is probably a hydroxyisopropylamide of lysergic acid.<sup>20</sup> It is related to an isomeric new ergot alkaloid, ergometrinine, of which it is a transformation product. This relationship recalls the isomeric interconvertible pairs ergotamine—ergotaminine and ergotoxine—ergotinine.<sup>22</sup>

The most notable advances in our knowledge of the structure of the ergot bases have come from the study of the products of hydrolysis. Ergotinine,  $C_{35}H_{39}O_5N_5$ , yields on alkaline hydrolysis ammonia, lysergic acid ( $C_{16}H_{16}O_2N_2$ ), isobutyrylformic acid, and what appears

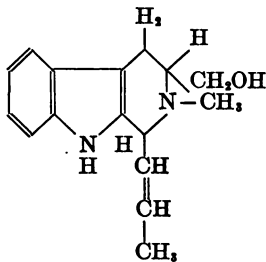
to be a peptide fraction, which can be further hydrolyzed to proline and nearly inactive phenylalanine.<sup>23, 24</sup> Isobutyrylformic acid, as the amide, was obtained many years ago from destructive distillation of ergotinine,<sup>25</sup> and it is now certain that the degradation product previously known as ergine,  $C_{16}H_{17}ON_3$ , is the amide of lysergic acid.<sup>26, 27</sup> In acid hydrolysis of ergotinine, on the other hand, Jacobs and Craig find that the lysergic acid portion of the molecule is destroyed, and the identifiable fragments are *l*-phenylalanine, *d*-proline methyl ester (after esterification), and a peptide of proline and phenylalanine.<sup>24, 28</sup>

Reductive hydrolysis of ergotinine, with sodium in amyl or butyl alcohol, has been very productive. In addition to dihydrolysergic acid,  $C_{16}H_{18}O_2N_2$ , the isomeric  $\alpha$  and  $\beta$ -dihydrolysergols,  $C_{16}H_{20}ON_2$ , are formed (provisional formula II), probably by reduction of the lysergic acid carboxyl group. With these is found proline methyl ester and a series of bases, designated as Bases II, IV, V, and VI.<sup>29</sup> Base II,  $C_{14}H_{20}N_2$ , is suggested to be a piperazine resulting from reduction of propylphenylalanine anhydride; Base IV is probably a substituted piperazine,  $C_{10}H_{18}N_2$ , from reduction of proline anhydride; Base V,  $C_5H_{11}ON$ , is a hydroxyamine and may be formed by reduction of proline or its ester to  $\alpha$ -pyrrolidyl carbinol; Base VI is a phenylpropanolamine, perhaps derived from phenylalanine and probably represents the portion of the ergotinine molecule that yields benzoic or *p*-nitrobenzoic acid in nitric acid oxidations. Ergotinine and, therefore, ergotoxine appear to be built up of lysergic acid or its amide, ergine, with proline, phenylalanine, and isobutyrylformic acid.<sup>29, 30, 31</sup>

Reductive hydrolysis of lysergic acid methyl ester gives dihydrolysergic acid and the epimeric dihydrolysergols, but none of the above-mentioned bases, whence it may be inferred that these bases are derived from the extra-lysergic acid portions of the ergotinine molecule.<sup>29</sup> The degradation fraction, lysergic acid, characteristic of all the ergot alkaloids thus far examined by Jacobs and Craig, appears to be a 4-carboline type, carrying a carboxyl, *N*-methyl, and propylene group, for which formula (I) has been advanced tentatively.<sup>32</sup> The nature of the tricarboxylic acid  $C_{14}H_9O_8N$ , and of the acid  $C_{13}H_8O_8N_2$ , arising from nitric acid oxidation of ergotinine and lysergic acid, respectively, is still unknown.<sup>30, 33</sup> The provisional structure suggested for lysergic acid,



(I) Lysergic acid



(II) Epimeric dihydrolysergols

3-propenyl-4-methyl-3,4-dihydro-4-carboline-5-carboxylic acid, has already led to the synthesis of similar compounds, e. g., of 3,4,5,6-tetrahydro-4-carboline-5-carboxylic acid and its derivatives, from condensation of tryptophane and formaldehyde or other aldehydes.<sup>34</sup> Ergoclavine, on alkaline hydrolysis, yields ammonia, lysergic acid, isobutyrylformic acid, and leucine, while on acid hydrolysis fractions are obtained, which may consist of racemized leucine and hydroxyproline.<sup>28</sup>

With the recognition of the new ergot alkaloid as the most important oxytocic principle of ergot, the question of assay and standardization arises<sup>19, 35</sup> and may affect the value of some of the recent publications on ergot assay.<sup>36-43</sup> The ergot base ergothioneine, long known to be present in the blood of the pig, has now been found in urine.<sup>44</sup> The effect of ergotamine tartrate on cerebral circulation has been studied.<sup>45</sup>

**Physostigmine.** A complete synthesis of physostigmine<sup>46</sup> (eserine), based on preliminary syntheses of *dl*-desoxyeseroline<sup>47, 48</sup> and *dl*-eserethole<sup>49</sup> has been accomplished by Julian and Pikl. *N*-Methylphenetidine was condensed with  $\alpha$ -bromopropionyl bromide, and the resulting analide converted to 1,3-dimethyl-5-hydroxyindole by heating with aluminum chloride. After ethylation, this product was condensed with chloroacetonitrile and reduced at the nitrile group to the primary amine, 1,3-dimethyl-3- $\beta$ -aminoethyl-5-ethoxyoxindole. The amino group was methylated by Decker's method, and the methylamino compound then resolved with *d*-camphorsulfonic and *d*-tartaric acids. The levo form, reduced with sodium and alcohol, gave *l*-eserethole, identical with that derived from physostigmine. By dealkylation to *l*-eseroline and treatment with methylisocyanate, *l*-physostigmine was obtained.<sup>46</sup> Antagonistic action of physostigmine with barbiturates and with nicotine has been studied.<sup>50</sup>

**Vasicine.** In an attack on the structural problem of vasicine (peganine), the 4-hydroxy-3-allyl-3,4-dihydroquinazoline formula suggested by Späth and Nikawitz<sup>51</sup> was first shown to be incorrect by synthesis of 3-allyl-3,4-dihydroquinazoline, which proved to be different from desoxyvasicine.<sup>52</sup> The correct desoxyvasicine formula was demonstrated to be 2,3-trimethylene-3,4-dihydroquinazoline by synthesis,<sup>53</sup> establishing the vasicine skeleton. The 4-keto derivatives of vasicine and of desoxyvasicine were prepared by oxidation, and 4-ketodesoxyvasicine synthesized for structural proof. Oxidized desoxyvasicine yielded with lead tetraacetate a hydroxy derivative identical with oxidized vasicine, a fact indicating that the vasicine hydroxyl group is on the methylene group attached to the 2-carbon atom.<sup>54</sup> This conclusion is confirmed by the complete vasicine synthesis of Späth.<sup>55</sup>

**Nicotine Types.** Investigations concerned with the existence of a toxifore grouping in nicotine have led to improved methods for the synthesis of nornicotine and nicotine.<sup>56</sup>  $\alpha$ -Substituted-*N*-methylpyrrolidines can be prepared in good yields by the application of suitable reduction methods to the corresponding  $\alpha$ -substituted-*N*-methylpyrrolines.<sup>57, 58</sup> The toxicity of a number of these compounds for goldfish

and in insect sprays has been compared; the most negative  $\alpha$ -substituents cause the greatest increase in toxicity.  $\alpha$ -Nicotine [ $\alpha$ -( $\alpha$ -pyrrolidyl)-*N*-methylpyrrolidine] and  $\alpha$ -nornicotine were likewise synthesized for these toxicity studies.<sup>59, 60</sup> The observation that partial detoxication of nicotine occurs during ultraviolet irradiation has been confirmed, but over-radiation restores the toxicity. No reasonable amount of irradiation will detoxify nicotine.<sup>61, 62</sup> Attempts to dehydrogenate nicotine with sulfur in boiling toluene resulted in the formation of thiodinicotyrine, together with a small amount of nicotyrine.<sup>63</sup> Anabasine ( $\beta$ -pyridyl- $\alpha$ -piperidine) has been found in *Nicotiana glauca* R. Grah. in amounts up to one percent<sup>64</sup> and the wild plant may serve as a good source of this valuable insecticide. The physical constants of very pure anabasine have been carefully measured,<sup>65</sup> and several investigations have been conducted on the pharmacological action and toxicity of anabasine and nicotine.<sup>66-70</sup>

**Cinchona Alkaloids.** In the cinchona group an interesting search is being made at the Mellon Institute for derivatives of cinchona alkaloids which may be less toxic and more effective than optochin in the treatment of pneumonia. A large number of compounds have been prepared and examined for pneumococcal value. Isoquinine and hydroxyethylhydrocupreine are less toxic than optochin, and are moderately effective.<sup>71</sup> Ethylapoquinine has given some favorable results,<sup>72</sup> indicating that the apoquinine series may be important. The  $\alpha$ - and  $\beta$ -apocupreines have been prepared by treatment of quinine with hydrochloric and sulfuric acids; they show a fairly high pneumococcal effect *in vitro*, and a protective power in mice similar to that of optochin, together with low toxicity.<sup>73</sup> A conversion of several cinchona alkaloids to the corresponding cinchona ketones by the action of sodium amide has been reported.<sup>74</sup> The form and optical properties of the crystals of a large number of cinchonine salts,<sup>75</sup> and the solubilities of cinchonine derivatives<sup>76</sup> have been studied. Quinine sulfate is found to crystallize with eight molecules of water, but this form is unstable and gradually breaks down to the dihydrate. No evidence is found for the existence of the previously-reported heptahydrate.<sup>77-79</sup> The frequent adulteration of illicit narcotics with cinchonine and strychnine has necessitated the development of methods for the separation and identification of these two alkaloids in such mixtures.<sup>80, 81</sup>

**Opium Alkaloids.** The research units engaged with the problem of addiction to the drugs of the morphine group have reported some progress on the study of the relationship between constitution and physiological action.<sup>82</sup> By the application of special hydrogenation technique to the morphine and codeine isomers of the pseudocodeine type, the dihydro derivatives of  $\beta$ - and  $\gamma$ -isomorphines,<sup>83, 84</sup> of pseudo- and allopseudo-codeines,<sup>85, 86</sup> and of pseudocodeine methyl ether<sup>87</sup> have been made available for pharmacological study. The comparison of sixteen closely related drugs is thus possible, for observation of the pharmacodynamic result of methylation of the phenolic hydroxyl, of

saturation of the alicyclic double bond, and of changes in position or configuration of the alcoholic hydroxyl. The effect of these changes on blood pressure,<sup>88, 89</sup> on respiration,<sup>90, 91</sup> on intestinal action,<sup>92-95</sup> as well as on toxicity, analgesia, and general depressant action has been measured.<sup>96-98</sup> The general similarity of the two drugs codeine and allopseudocodeine, and of the pair isocodeine and pseudocodeine in respect to physiological action leads to the conclusion that in the first-named pair of positional isomers, the alcoholic hydroxyl probably has the same configuration and in the last-named pair, the opposite configuration.

Extensive studies have been carried out to ascertain the part played by the alcohol hydroxyl group in the picture of morphine physiological action. To this end, compounds were prepared in which the alcoholic group of morphine and codeine, or the isomers and their dihydro derivatives, was covered by a methyl<sup>99</sup> or acetyl group, converted to a carbonyl group,<sup>100</sup> or replaced entirely by hydrogen.<sup>101-104</sup> The inevitable conclusion reached from the investigation of a considerable series of such derivatives is that the alcoholic hydroxyl group as present in the morphine series exerts an inhibiting influence with respect to most physiological effects. With its replacement or conversion to another chemical type, marked increase in toxicity, general depression, and especially analgesia is seen, combined with a decrease in emetic effect. The maximum narcotic effect is realized in drugs having the free phenolic hydroxyl and a masked or eliminated alcoholic hydroxyl, as desoxycodine-C, dihydrodesoxymorphine-D, heterocodeine, dihydroheterocodeine,  $\alpha$ -acetylmorphine, and dihydromorphinone.<sup>105-111</sup> Information concerning the relative importance of groups located at 6- and 8-positions in the morphine molecule, with elimination of the influence of asymmetry at these points has been obtained through the study of the isomeric pairs, dihydrocodeinone (Dicodid) and dihydropseudocodeinone, dihydromorphinone (Dilaudid) and dihydroisomorphinone. Comparison of the physiological action of these substances leads to the conclusion that a functional group located on C-6 is in some respects about ten times as effective as the same group on C-8.<sup>100</sup> The presence of the tertiary nitrogen atom of morphine and codeine seems to be essential for the typical morphine effects. Transformation to the quaternary ammonium salts results in a marked diminution in pharmacological action, and in the appearance of the well-known curare-like action of quaternary ammonium compounds.<sup>112</sup> While an extensive discussion of non-alkaloidal material can not be included in this review, attention should be drawn to the fact that several of the phenanthrene derivatives synthesized by Mosettig and his co-workers show a surprising similarity in effect to some of the morphine derivatives.<sup>82, 113</sup> It should be especially noted that the physiological effectiveness characteristic of groups in the 3- and 6-positions of the morphine molecule is likewise observed in the phenanthrene series, and the changes in physiological action resulting from modifi-



cation of such groups in the morphine series are roughly paralleled in the phenanthrene derivatives.

The researches on the preparation of morphine substitutes have long since reached the stage where the development of reliable clinical methods for determining the degree of tolerance and addiction in man is imperative. This phase of the work is being conducted by the United States Public Health Service. In this connection the addiction liability of codeine, isocodeine, pseudocodeine, and Dilaudid has been studied; all of these drugs are found to be definitely habit-forming in man.<sup>114-116</sup>

Gross and Pierce conclude from the effects of morphine on the oxygen consumption of brain tissue that morphine administered subcutaneously stimulates rather than depresses brain metabolism.<sup>117</sup> Numerous investigations have been carried out on excretion,<sup>118, 119</sup> tolerance,<sup>120, 121</sup> and the effect of morphine on circulation, intestinal activity, and acidosis,<sup>122-125</sup> and the effect of Dilaudid on the intestine has likewise been rather extensively studied.<sup>124, 126-129</sup>

Reduction of pseudocodeine electrolytically or with sodium in alcohol, yields the phenolic isomers dihydropseudocodeine-B and -C, respectively. These isomers differ only in the location of the alicyclic unsaturation, and can be degraded to the corresponding isomeric methine bases.<sup>130</sup> The mechanism advanced to account for the appearance of these isomers led to the search for analogous isomers in the supposedly homogeneous reduction product from desoxycodine-C and  $\alpha$ -chlorocodine, namely, dihydrodesoxycodine-A. It could be demonstrated that this substance consists of a mixture of dihydrodesoxycodines -B and -C, differing likewise only in the location of the unsaturated linkage, and crystallizing together in practically constant proportion.<sup>131</sup>

The alkylthiocodides are formed by mercaptolysis of the halogenocodides, a process parallel to the hydrolysis of these compounds.  $\alpha$ -Ethylthiocodide undergoes an internal rearrangement to the phenolic  $\beta$ -ethylthiocodide, a reaction demonstrably analogous to the rearrangement of codeine methyl ether to thebainone methyl enolate.  $\beta$ -Ethylthiocodide and thebainone methyl enolate both undergo hydrolysis to the true thebainone. The so-called  $\gamma$ -ethylthiocodide is in reality only an oxide of  $\beta$ -ethylthiocodide, and  $\delta$ -ethylthiocodide is an ethylthio analog of pseudocodeine methyl ether.<sup>132</sup> The metathebainone question has been studied with the object of obtaining positive evidence for the Schöpf formula. The series of metathebainone reduction products obtained supports the 9,14-position postulated for the ethanamine side chain, the synthesis of a tetrahydrodesoxymetacodine different from tetrahydrodesoxycodine being particularly convincing.<sup>133</sup>

The structure of pseudomorphine is one of the problems of morphine chemistry that still awaits final solution, and upon which investigation is still in progress. As a step in this direction, the oxidation of phenolic bases of the morphine series was undertaken.  $\alpha$ -,  $\beta$ -,  $\gamma$ -Isomorphines, dihydro- $\gamma$ -isomorphine, dihydromorphine, heterocodeine, and

dihydrodesoxymorphine-D yield dimolecular oxidation products similar to pseudomorphine. The point of union of the two nuclei still awaits demonstration.<sup>134</sup> It is quite certain that any of the morphine substitutes used in medical practice having the free (or easily freed) phenolic hydroxyl group, as Dilaudid or heroin, will give dimolecular products of similar properties, so that specific tests for morphine relying on pseudomorphine formation can be used only with caution. Tests for pseudomorphine, preparative methods, and pharmacological data have been published.<sup>135, 136</sup> The need for large quantities of morphenol or methylmorphenol for the study of the physiological action of simple substitution products (especially amino alcohols) has led to the development of a greatly improved technique for the degradation of morphine, of which the unique feature is the decomposition of  $\alpha$ - or  $\beta$ -methylmorphimethines in the presence of sodium cyclohexanolate.<sup>137</sup> A large number of salts of codeine with benzoic acid and its derivatives have been prepared and described, and may be added to the already very numerous known salts of this important alkaloid.<sup>138</sup> A similar series of benzoates of strychnine has likewise been published.<sup>139</sup> Codeine phosphate, crystallized from water, consists entirely of the sesquihydrate.<sup>140</sup>

The opium alkaloids, narceine and narcotine, have been reinvestigated, especially with the view of verifying the identity of opium narceine with that prepared from narcotine quaternary alkylates. The results obtained confirm this identity, and indicate that the generally accepted substituted desoxybenzoin formula for narceine is correct.<sup>141</sup> A study of the hydrolysis, alcoholysis, and ammonolysis of narcotine and hydrastine alkyl salts has led to the proposal of a new mechanism to explain these reactions. The mechanism advanced, which involves formation of a highly unstable intermediate resulting from opening of two rings in the quaternary ammonium salt, is supported by the fact that the reaction between narcotine methyl salts and HA reagents always produces salts of narceine derivatives.<sup>142</sup> New contributions to the pharmacology of narcotine<sup>143</sup> and hydrastine and related alkaloids<sup>144</sup> have appeared.

Several assay procedures have been reported for opium;<sup>145-147</sup> the International Committee method appears to be less satisfactory in several respects than the Group Committee method recommended for adoption in U. S. P. XI. Analytical procedures for the detection of very small amounts of morphine and heroin have been worked out, especially for these drugs in saliva ("race horse doping") and in the notorious "Red Pills" which have lately appeared in the illicit narcotic market.<sup>148-152</sup>

**Miscellaneous Alkaloids.** A new synthesis of racemic pseudoephedrine, based on the  $\alpha$ ,  $\beta$ -dibromoether synthesis of Boord, has been developed, and provides a good method for the preparation of an extended series of substituted ephedrine derivatives.<sup>153</sup> An investigation of the crystalline forms of ephedrine shows it to exist in an anhy-

drous form of m. p.  $38.1^{\circ}$ , and as a hemihydrate of m. p.  $40^{\circ}$ . The two forms give a eutectic mixture melting at  $32.1^{\circ}$ .<sup>154</sup> The effect of ephedrine on coronary circulation<sup>155</sup> and on spinal reflexes of monkeys<sup>156</sup> has been described.

Additional evidence for the cuscohygrine formula is found in the fact that synthetic ethyl-1-methyl-2-pyrrolidine acetate is identical with ethylhomohygrinate. This, together with the observation that cuscohygrine does not react with benzaldehyde and gives no iodoform test,<sup>157</sup> seems to confirm the *sym*-bis-(1-methylpyrrolidyl) acetone cuscohygrine formula of Liebermann and Cybulski.

A number of esters of yohimbic acid, the hydrolysis product from yohimbine, have been described, in particular, esters with ethylene-glycol, trimethyleneglycol, glycerol, ethylenechlorohydrin, trimethylene chlorohydrin, and cetyl and benzyl alcohols.<sup>158, 159</sup> Weinberg<sup>160</sup> has studied the pressor action of yohimbine and quebrachine.

In the caffeine series a variety of new 8-ethers have been prepared from 8-chloro- and 8-bromocaffeine.<sup>161</sup> Several of these were converted by the method of Biltz to the corresponding trimethyl-9-substituted uric acids.<sup>162</sup> Utilizing the acid anhydride method of Boehringer Sons, 8-alkylcaffeines were prepared by replacing the 8-hydrogen with alkoxyl and heating with the acid anhydride containing the desired alkyl residue.<sup>163</sup>

Assay procedures, which can be only mentioned here, have been published for cinchona,<sup>164</sup> hyoscyamus,<sup>165-167</sup> Ma Huang,<sup>168</sup> Washington belladonna,<sup>169</sup> and for strychnine alkaloids in strychnine sulfate.<sup>170</sup> Among analytical methods may be cited those for cocaine in the presence of procaine,<sup>171, 172</sup> for strychnine and brucine as hydroferrocyanides or dichromates,<sup>173, 174</sup> for the aconite alkaloids,<sup>175, 176</sup> and for ephedrine,<sup>177</sup> as well as general analytical procedures and reagents applicable to whole groups of alkaloids.<sup>178-185</sup> See also under the opium alkaloids.

**New Alkaloids.** From *Lupinus Corymbosis* Heller a new alkaloid, hexalupine,  $C_{15}H_{20}ON_2$ , has been isolated. *Lupinus Palmeri* S. Wats. yields lupinine and the new bases tetralupine,  $C_{10}H_{19}ON$ , and pentalupine,  $C_{16}H_{30}ON_2$ .<sup>186</sup> The toxic principle of *Crotalaria spectabilis* Roth has been identified as an alkaloid, monocrotaline, to which the formula  $C_{16}H_{26}O_6N$  is tentatively assigned.<sup>187</sup> The Chinese drug han-fang-chi, probably from *Cocculus japonicus* (Hoffman and Schultes), a diuretic and cathartic, contains about two percent of alkaloids, the main constituent being  $C_{38}H_{42}O_6N_2$ , probably identical with tetrandine.<sup>188</sup> The tonic and antipyretic drug chin-shih-hu, a mixture of several *Dendrobium* species contains (Szechuan variety) chiefly dendrobine,  $C_{16}H_{25}O_2N$ , an alkaloid having a slight antipyretic and depressor action.<sup>189, 190</sup> The pharmacological action of peimine and peiminine, first isolated in 1932 from the drug Pei Mu, has been investigated.<sup>191</sup> From *Ceanothus velutinus* bark a new alkaloid,  $C_{23}H_{26}O_4N_2$ , has been obtained.<sup>192</sup> *Coptis occidentalis* Salisbury (Western Golden-

thread) is found to contain about the same amounts of coptine and berberine as *Coptis trifolia*, and is a more abundant source of these alkaloids.<sup>193</sup> Investigation of *Datura innoxia* Miller shows it to contain only *l*-scopolamine.<sup>194</sup> From wu chü yü (*Evodia rutaecarpa*), in addition to the known alkaloids rutaecarpine and evodiamine, the new base wuchuyine,  $C_{13}H_{13}O_2N$ , has been isolated. The indifferent compound evodin, for which Keimatsu found  $C_{18}H_{22}O_6$ , appears to have the formula  $C_{26}H_{30}O_8$ .<sup>195</sup>

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# Chapter XVI.

## Food Chemistry.

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**Arrangement of this Review.** We here take up, first, the individual chemical entities important in foods; second, chemical investigations of food commodities; and, finally, investigations of certain relations of food to health and longevity, in some of which the experimental variables have been individual elements and in others have been natural articles of food.

**Carbohydrates and their Enzymes.** Continuing their well-known investigations, Taylor<sup>1, 2</sup> has contributed further to the chemistry of starch; Caldwell<sup>3, 4</sup> to the chemistry of the amylases; and Nelson<sup>5</sup> to that of the invertases (sucrases). Kertesz<sup>6, 7</sup> has studied the relations of viscosity and water concentration to invertase action. Spoehr and Milner<sup>8</sup> have entered a practically new area of research in their studies of the starches of leaves, the first results of which have appeared toward the end of the year under review. Bendaña and Lewis<sup>9</sup> find inulin to be utilized, by the growing rat, as a supplementary source of energy; but distinctly inferior to sucrose or fructose as a sole dietary carbohydrate.  $\beta$ -Lactose has been officially "accepted" by the American Medical Association;<sup>10</sup> and Cajori<sup>11</sup> has determined a number of the properties of intestinal lactase.

The nutritive value of lactose in man has been studied, from the viewpoints both of the normal chemistry of nutrition and of medicine, by Koehler, Rapp, and Hill.<sup>12</sup>

In comparisons of the nutritional responses to different sugars, the year has brought interesting reports. Feyder,<sup>13</sup> experimenting with rats, found that sucrose has a significantly greater fattening effect than dextrose; and Whittier, Cary, and Ellis<sup>14</sup> (who employed both rats and pigs) found that lactose was less fattening than sucrose and more favorable both to growth and longevity. Carruthers and Lee<sup>15</sup> find maltose to be the main product of the action of muscle amylase upon glycogen. Olmsted, Curtis, and Timm<sup>16</sup> have studied the feeding of pentosans and cellulose (fiber) to man.

**Fats, Lipoids, and Lipases.** Hughes and Wimmer<sup>17</sup> find no increase in the amount of soluble, volatile fatty acids present as glycerides in the thoracic lymph during the digestion of fats which contain such acids, indicating that the utilization of these acids as food follows

a different path from that of the insoluble fatty acids. Lepkovsky, Ouer, and Evans<sup>18</sup> found that, when lard was saponified and its distilled fatty acids esterified with glycerol to form "synthetic" lard, this was as satisfactory for the normal growth of rats as the original lard, whether fed as 25 or 60 percent of the diet. When the free fatty acids were fed alone or merely mixed with glycerol the results were good at the 25 percent, but somewhat inferior at the 60 percent level. The methyl and ethyl esters were satisfactory substitutes for the glycerides at the lower but not at the higher level.

Using the rat as experimental animal, Olcott, Anderson, and Mendel<sup>19</sup> have studied the influence of cereal diets upon the composition of the body fat.

Ward, Lockwood, May, and Herrick<sup>20</sup> have described the production of fat from glucose by molds, and especially the large-scale cultivation of *Penicillium javanicum* for this purpose.

Hileman and Courtney<sup>21</sup> have studied the seasonal variations in lipase content of milk.

Mattill and Olcott<sup>22</sup> have continued their investigation of antioxidants and the autooxidation of fats. Weber and King<sup>23</sup> have studied the specificity and inhibition characteristics of liver esterase and of pancreatic lipase. Sure, Kik, and Buchanan<sup>24</sup> find that a deficiency of vitamin B or of the vitamin B complex markedly reduces the lipase and esterase activity of pancreas extracts. Falk and McGuire<sup>25</sup> find patterns of relative hydrolyzing actions upon ten esters which are different for the lung tissues of normal and of rachitic rats, whereas no corresponding differences were found in kidney or liver tissues. Boyd<sup>26</sup> finds that in man the taking of food under normal conditions does not cause great variations in the concentration of plasma lipids.

Schoenheimer and Rittenberg have prepared stearic acid 6-7-9-10-d<sub>4</sub> from linoleic acid and deuterium,<sup>27</sup> described methods of following its fate in the body,<sup>28</sup> and shown that the fatty acid radicals thus tagged with heavy hydrogen were largely carried to the fat depots before undergoing catabolism.<sup>29</sup> Similarly, coprostanone 4-5-d<sub>2</sub> has been prepared and studied as an intermediate in sterol metabolism.<sup>30</sup>

Sinclair has continued his studies of the phospholipids and found relatively constant ratios of solid to liquid fatty acids, regardless of the degree of unsaturation of the mixed acids, this depending upon the relative proportions of the different unsaturated fatty acids present.<sup>31</sup> He also finds further evidence of the selection and retention of unsaturated fatty acids by the phospholipids of animal tissues;<sup>32</sup> and of the existence in the body of at least two classes of phospholipids: (1) those essential to the structure of the cell, and (2) those functioning as intermediates in the metabolism of fat. The former tend to contain the more highly unsaturated, the latter the less highly unsaturated, fatty acids.<sup>33</sup>

**Amino Acids, Food Proteins and Proteases.** The "unknown essential amino acid" of Rose and his coworkers is now<sup>34, 35, 36</sup>



reported to be an  $\alpha$ -amino- $\beta$ -hydroxybutyric acid; the second "unknown essential" referred to in previous work was found to be isoleucine. Citrulline and hydroxyglutamic acid are definitely shown to be non-essential, since satisfactory growth has been secured on highly purified diets devoid of both of these amino acids.

The observation of Boyd and Mover<sup>37</sup> that more diazotized arsanilic acid couples with proteins than can be accounted for by the histidine and tyrosine present, remains unexplained; the isolation (McMeekin<sup>38</sup>) from hydrolyzed protein of a blood pressure depressing material, which gives a positive diazo reaction, but is apparently not histamine or histidine, may have some bearing on this question.

The use of potassium trioxalatochromiate,  $[\text{Cr}(\text{C}_2\text{O}_4)_3\text{K}_3]$ , as a specific precipitant for glycine,<sup>39</sup> and of rhodanilic acid,  $[\text{Cr}(\text{CNS})_4 \cdot (\text{C}_6\text{H}_5\text{NH}_2)_2\text{H}]$ , for proline,<sup>40</sup> has enabled Bergmann<sup>40</sup> to speculate concerning the structure of gelatin. Patton<sup>41</sup> reports new data on the glycine contents of a large number of proteins, as determined by the colorimetric method which he has developed.

The sulfur-containing amino acids continue to be the subject of extensive researches in many laboratories, both from the viewpoint of their structural significance in proteins generally and in specific substances of special biological interest, and in their rather unique interrelationships as indispensable dietary factors. Evidence for the existence in proteins of at least two other forms of sulfur than cystine and methionine has been discussed by Blumenthal and Clarke<sup>42</sup>; one of these yields sulfate on treatment with bromine water, and sulfide with alkaline plumbite, while the other yields sulfate on boiling with nitric acid, but fails to respond to plumbite.

A number of sulfur-containing compounds of interest have been synthesized by du Vigneaud and his associates; crystalline cystinyldiglycine and benzylcystinyglycine have been obtained and their identity with the products isolated from glutathione has been proved<sup>43</sup>; homocysteine has been crystallized and converted into the corresponding thiolactone<sup>44</sup>; a new synthesis for homocystine, not involving costly methionine as starting material, has been described<sup>45</sup>; and this substance has been resolved into the optically active isomers and their configurational relationship to naturally occurring methionine established.<sup>46</sup>

The next higher homologs of homocystine and methionine, pentocystine and homomethionine, respectively, are entirely ineffective in replacing cystine for growth,<sup>47</sup> as are also dithioethylamine,<sup>48</sup> and the hydantoins and phenylhydantoins of cystine and cysteic acid.<sup>49</sup> Dibenzoylcystine appeared to show some value for growth on a cystine-deficient diet.<sup>49</sup> Although *d*-cystine appears wholly ineffective in replacing *l*-cystine in nutrition, Dyer and du Vigneaud<sup>50</sup> found that both *d*- and *l*-homocystine supported growth in rats on a cystine-deficient diet; and Stekol<sup>51</sup> observed that *l*- and *dl*-methionine were equally well retained in adult and growing dogs.

White and Jackson<sup>52</sup> found that the feeding of bromobenzene to rats in addition to an otherwise growth-promoting diet results in growth cessation analogous to that on a cystine-deficient diet; additional supplements of cystine or methionine, but not of taurine or sodium sulfate, permit resumption of growth. The rat is shown to detoxicate bromobenzene with the formation of *p*-bromophenylmercapturic acid. Medes<sup>53</sup> presents contributory evidence for the theory that cystine sulfide may be an intermediate in the metabolism of cystine. Brand, Cahill, and their associates<sup>54, 55, 56</sup> have studied the effect of various amino acids on the cystine excretion of a cystinuric. A normal cystine content of the hair and nails of cystinurics was reported by Lewis and Frayser<sup>57</sup>; Hess<sup>58</sup> found an abnormally low cystine value in the nails of arthritic individuals.

Gordon and Jackson<sup>59</sup> report that amino-*N*-methyltryptophane can support growth in rats on a tryptophane-deficient diet, while Bz-3-methyltryptophane and Pr-2-methyltryptophane are without appreciable effect.

Butts, Dunn, and Hallman<sup>60</sup> observed both a glycogenic and a ketolytic action following administration to rats of *D*-alanine, *DL*-alanine, and glycine, the effectiveness of the amino acids in both respects decreasing in the order named.

Borsook and Jeffreys<sup>61</sup> have adapted the Warburg technique to the study of the intermediary metabolism of mixtures of natural amino acids by surviving slices of rat liver, kidney, diaphragm, spleen, and small intestine; space does not permit mention of their interesting and significant findings.

With the discovery that phenylalanine and proline are constituents of crystalline insulin,<sup>62</sup> Jensen and his coworkers have accounted for practically all of the molecule, without obtaining any indication of a prosthetic group which might explain the unique physiological activity of this protein. After treatment of the hormone with phenylisocyanate or with  $\alpha$ -naphthylisocyanate, only five percent of the potency remains, although the sulfur and cystine values are unchanged.<sup>62</sup> The inactivation by sulfhydryl compounds and by metallic derivatives has also been studied.<sup>63</sup>

Kunitz and Northrop<sup>64</sup> report the isolation from pancreas of a new crystalline zymogen, *chymotrypsinogen*, changed by crystalline trypsin (but not by enterokinase) to an active proteolytic enzyme, *chymotrypsin*, which has also been crystallized and which differs somewhat in its enzymatic behavior from crystalline trypsin. Both of these new products seem to be pure proteins, in which the activity is a property of the protein molecule.

Contrary to the old theory that long chain peptides are the major products of the action of pepsin on proteins, Calvery<sup>65, 66</sup> has confirmed his earlier observation that the enzyme (in 8 to 40 days) can hydrolyze about one-third of the peptide linkages in crystalline egg albumin, and

he has shown that free amino acids and dipeptides are among the split products.

Methods for the preparation and assay of trypsinogen and enterokinase are discussed by Bates and Koch,<sup>67</sup> who conclude that enterokinase behaves as a catalyst in activating trypsinogen. Cohn and White,<sup>68</sup> in studying the hydrolysis by pepsin and by trypsin of heat-treated and raw egg white, obtained indications that the latter contained an anti-tryptic agent. Sure, *et al.*<sup>69, 70</sup> report a technique for the estimation of the tryptic-ereptic activity of pancreatic and intestinal extracts of the rat; and note that this activity is unimpaired in deficiency of vitamin B or of the vitamin B complex.

The chemical and configurational requirements for the substrate in dipeptidase action have been defined by Bergmann, *et al.*,<sup>71</sup> who discuss in detail a theory for the mechanism of dipeptidase action. Natural papain has been shown to contain two proteolytic systems, a *proteinase* and a new *polypeptidase*, the former being reversibly inactivated by oxidation, the latter irreversibly inactivated.<sup>72</sup> The substrate requirements of the polypeptidase, which have been studied in detail with a large number of synthetic peptides, differentiate this enzyme from the already known dipeptidase, aminopolypeptidase, and carboxypolypeptidase.<sup>73, 74</sup>

*Tyrosinase* has been studied by Graubard and Nelson,<sup>75, 76</sup> who define a new unit of activity and present evidence that the same enzyme catalyzes the oxidation of both mono- and di-hydric phenols. The activation of *arginase* by metals has been studied by Hellerman and Perkins,<sup>77</sup> who have also observed hydrolysis of arginine in the absence of arginase by crystalline urease with suitable metallic ions.

*Quantitative aspects of the nutritive efficiency of proteins and of the protein requirement in nutrition.* While space does not permit of its full discussion here, mention should be made of the extended work of Smuts<sup>78</sup> (under the direction of, and prepared for publication by, H. H. Mitchell at the University of Illinois) upon the relation between the basal energy metabolism and the endogenous nitrogen metabolism, with particular reference to the estimation of the maintenance requirement for protein. In the same laboratory, the metabolic nitrogen of the feces of the rat, swine, and man has been investigated by Schneider<sup>79</sup> from the viewpoint of dividing it into a "digestive fraction," which varies directly with the quantity of food consumed, and the true "endogenous nitrogen," which is independent of the food consumed. Mason and Palmer<sup>80</sup> report comparative experiments upon the nutritional efficiency of casein, gelatin, and zein for maintenance in adult rats. "The percentage retention (of nitrogen) calculated by McCollum's method averaged 74 for casein, 23 for gelatin, and 57 for zein. . . . The percentage retention increased as less protein was ingested, even though it was never fed above the endogenous level." The original article must be consulted for full interpretation. In a carefully controlled series of experiments, Forbes and his coworkers<sup>81</sup> observed a

progressively increasing efficiency of utilization of food energy for growth in rats as the percentage of protein (casein) in the diet was increased from 10 to 25 percent. Daggs and Tombouliau<sup>82</sup> find those proteins especially favorable to support lactation which furnish richly the constituents of glutathione. Csonka<sup>83</sup> has investigated the proteins of yeast and reports that "The cystine, tryptophane, histidine, and lysine content of yeast protein places it in a favorable position among those considered of good quality."

*Hematopoietic substances.* Substances of protein or polypeptide nature, whose special significance is related to hemoglobin and erythrocyte formation, are reviewed in connection with iron.

**Mineral Elements.** Variations in the intake of each of the common mineral elements during a prolonged series of balance experiments have been studied by Bassett and Van Alstine.<sup>84</sup> When the diet was kept constant in terms of the kinds and amounts of the articles of food used, the variations in intake from period to period were, in many cases, significantly larger than the variations in a series of analyses of the same sample, indicating that in metabolism balance experiments food should actually be analyzed for each balance period.

*Calcium and phosphorus.* Daniels and coworkers<sup>85</sup> have reported experiments from which they conclude that the calcium needs of normal children of preschool age can be met by foods furnishing 45 to 50 mg. of calcium per kilogram of body weight, or 7 to 9 mg. per centimeter of height, provided sufficient vitamin D is allowed; and that the phosphorus needs can be met with 60 to 70 mg. per kilogram, or 9 to 11 mg. per centimeter. Sherman and Campbell<sup>86</sup> have published the results of an extended series of experiments upon the effects of increasing the calcium content of a diet which had already been shown adequate in that it maintained normal growth, health, reproduction, and lactation through successive generations of rats. The enrichment of the calcium content from 0.2 percent to 0.35 percent of the dry food resulted in more efficient utilization of the food (whether calculated on the basis of its energy value or protein content), earlier maturity, and higher adult vitality, showing that the optimal intake is considerably higher than the "need."

Kohman and Sanborn<sup>87</sup> have reported preliminary indications that oxalates in foods act both to diminish the absorption of calcium from the digestive tract and to increase the body's loss of calcium in the urine. Simultaneously, Fincke and Sherman<sup>88</sup> investigated the quantitative nutritional availability of the calcium of milk, kale, and spinach. The calcium of milk was excellently utilized, and that of kale showed almost as high a percentage availability, while the calcium of spinach was utilized to only a very small extent, if at all. The unavailability of the calcium of spinach was not due to fiber, and was shown experimentally to be at least chiefly due to the oxalic acid or oxalates present.

Clinical cases of calcium deficiency in infancy and in childhood

have been reported by Nesbit<sup>89</sup>; and Newburgh<sup>90</sup> has emphasized the dependence of normal skeletal development upon the supply of calcium and phosphorus available to the fetus through the mother; while Campbell, Bessey, and Sherman<sup>91</sup> have shown how a low intake of food calcium, not recognizable as a deficiency in the first generation, may result in the deterioration and dying out of the family if continued too long.

*Iron and hematopoietic substances.* Vahlteich, Funnell, MacLeod, and Rose<sup>92</sup> find the iron of egg yolk and of bran, prepared for human consumption by steaming and toasting, to be equally effective for the maintenance of iron equilibrium in the human adult. These experiments also add to our knowledge of the quantities of iron needed in normal human nutrition. The data for one subject (a woman of 56 kilograms body weight) indicated a need of 6.0 mg. iron per day, or 0.11 mg. per kilogram. The other subject, weighing 71 kilograms, had a larger proportion of body fat and appeared to need only 6.1 mg., or 0.09 mg. per kilogram, per day. The iron requirement of the normal human adult has also been studied by Farrar and Goldhamer<sup>93</sup>; and the iron metabolism of preschool children, by Ascham.<sup>94</sup>

Orten, Smith, and Mendel,<sup>95</sup> in experiments with rats whose diet was relatively poor in mineral elements, found that an increase of the calcium allowance exerted a markedly favorable effect upon the iron economy and normal blood formation. Ellis and Bessey<sup>96</sup> have studied the effects of different diets upon the hemoglobin concentration of the blood in rats at one month and at one year of age.

Whipple and coworkers<sup>97</sup> have studied further the relative efficiencies of heart, kidney, liver, and spleen preparations in blood regeneration. They conclude that several factors, rather than a single hematopoietic factor, are concerned with regeneration after blood loss; and that this process should be distinguished sharply from that of recovery from pernicious anemia. In the same laboratory,<sup>98</sup> it was found possible, by adjustments and alternations of feeding and fasting periods, to vary the "metabolic path" taken by the nutrients and metabolites, with resulting differences in efficiency of hemoglobin formation, striking conservation of metabolized material being sometimes effected. Whipple<sup>99</sup> has also summarized both the most recent and the previous work of his laboratory upon hemoglobin regeneration as influenced by diet and other factors.

Dakin and West<sup>100</sup> have discussed the chemical nature of a hematopoietic substance isolated from liver, which has the properties of a hexosamine-peptide. Subbarow, Jacobson, and Fiske<sup>101</sup> have briefly reported the separation of two crystalline substances from liver, both of which are reticulocytogenic in guinea pigs and one of which is effective in the cure of experimental blacktongue in dogs.

*Iodine.* Holmes and Remington<sup>102</sup> find from 3,000 to 13,000 parts per billion of iodine in cod liver oil; and estimate that 10 cc. of cod liver oil, the daily amount recommended by the U. S. Pharmacopoeia, furnishes by itself about enough iodine to meet the daily needs of

normal nutrition. Coulson<sup>103</sup> finds 290 parts per billion of iodine in the meat of the *conch*, for which he gives the analysis (on the fresh basis): moisture 74.6, protein 18.6, fat 0.3, ash 1.7, calcium 0.089, phosphorus 0.112, magnesium 0.246, and sulfur 0.315 percent.

Holley, Pickett, and Brown<sup>104</sup> have studied the causes of variation in the iodine contents of vegetables.

*Other mineral elements.* McCollum and his coworkers<sup>105, 106</sup> have continued their investigation of *magnesium* as a nutritionally essential element; and Duncan, Huffman, and Robinson<sup>107</sup> have observed the development of tetany associated with low blood magnesium in calves reared on a milk diet.

Daniels and Everson<sup>108</sup> have found a dietary deficiency in *manganese* to be responsible for the congenital debility of the young of mothers reared on milk modified with copper and iron.

*Zinc* was found by Stirn, Elvehjem and Hart<sup>109</sup> to be indispensable to the normal nutrition of the rat.

The effects of diets deficient in mineral elements generally have been investigated further by Clarke and Smith,<sup>110</sup> and by Swanson, Timson, and Frazier.<sup>111</sup>

*Fluorine* toxicosis has been studied extensively by workers at the University of Wisconsin<sup>112-114</sup> and by Smith and Lantz.<sup>115</sup>

Franke and his associates<sup>116-120</sup> continue their investigation of poisoning by natural plant foodstuffs with an abnormally high *selenium* content.

**Vitamin A and Its Precursors.** Mackinney<sup>121</sup> has studied the carotenes of the leaves of 59 species of plants and found that  $\beta$ -carotene is the major fraction in all these cases, while in 40 of the 59 cases  $\alpha$ -carotene was found in proportions ranging from traces to 35 percent of the total carotene present. "Phylogenetic considerations have been applied with fair success in predicting that leaves of closely related plants or groups of plants will not differ materially in their carotene complexes." Strain<sup>122</sup> has made a further study of the carotenes from different sources and of the properties of  $\alpha$ - and  $\beta$ -carotene.

Treichler, Grimes, and Fraps<sup>123</sup> have studied the relation of the color and carotene content of butter fat to its vitamin A value, especially in the case of cows kept on rations consisting largely of white and yellow corn (maize), respectively. In both cases, transfer from pasture to the grain ration resulted in gradual decline both of the carotene content and of the vitamin A value of the milk fat, but to a less extent with yellow corn than with white corn. Their bulletin should be read in full by those interested in the subject.

Guilbert and Hart<sup>124</sup> have continued their studies of the vitamin A requirement of cattle and the storage of this vitamin and its precursor in the different parts of the body.

**Vitamin B Complex.** Following the preliminary report of Williams<sup>125</sup> suggesting the structure for vitamin B hydrochloride much

confirmatory evidence has appeared.<sup>126-133</sup> (See Chapter XIV for discussion.)

Some clinical observations with crystalline vitamin B<sub>1</sub> have been reported by Vorhaus, Williams, and Waterman,<sup>134</sup> who found strikingly beneficial results in a large number of cases of neuritis of various origin and in the small number of cases of "unexplained gastrointestinal hypotonia with anorexia" which they studied. These authors concluded that "there is evidence to suggest frequent deficiency of vitamin B<sub>1</sub> in the human dietary." Further studies, the details of which are not available, have indicated a beneficial effect of large doses of the vitamin in some cases of deranged carbohydrate metabolism.<sup>134, 135</sup>

Waterman and Ammerman<sup>136</sup> found that the administration to young rats on the Chase-Sherman diet of graduated doses of the crystalline vitamin up to 160 gamma per day (80 to 160 times that necessary for maintenance of life) resulted in progressive increases in the growth rate until "the growth at the higher levels of B dosage approaches the best obtainable with rich mixed diets (Yale)." There was thus no indication of requirement of a second heat-labile B factor; "A more probable explanation is that large amounts of B exercise a growth acceleration sometimes confused with that due to B<sub>4</sub>." Adult pigeons,<sup>137</sup> depleted of vitamin B on a diet of autoclaved whole wheat for three weeks, showed progressive increases in weight with supplements of 10 to 80 gamma per day of crystalline vitamin, but even with 160 gamma (40 times the amount required to cure polyneuritis) the "normal" weight (i. e., the weight before depletion) was not attained, although amounts of raw whole wheat containing not more than 50 to 60 gamma of vitamin B<sub>1</sub> restored the birds to normal weight. "The results reported furnish additional evidence that there is a B complex factor other than B (B<sub>1</sub>) needed for the complete nutrition of pigeons."

Members of Williams' group have also reported studies on the injection method of measuring the vitamin B values of purified preparations.<sup>138</sup>

The relative concentrations of vitamin B found by Brodie and MacLeod<sup>139</sup> in tissues from young adult rats reared on an "adequate" diet were roughly as follows: liver 10, heart 10, kidney 5, brain 3, and muscle 1. Spleen, lung, and blood showed only traces of the vitamin. The stores in some organs could be significantly increased by fortifying the diet with brewers' yeast. After animals had been maintained for four to five weeks on a depletion diet, the presence of vitamin B could not be demonstrated in any organ except the brain. In accordance with this work, Griffith<sup>140</sup> found that the body stores of vitamin B were readily depleted when rats were fed a B-deficient diet; on the other hand, even after 100 days on a G-deficient diet, the tissues still contained much vitamin G. Evans and Lepkovsky<sup>141</sup> noted a definite sparing effect of high-fat diets on the vitamin B content of the liver, muscle, and brain of rats reared on a diet deficient in vitamin B. A marked depletion of the absolute amount of the vitamin present in the liver was

noted under conditions in which but little loss occurred from the muscles, indicating that "the liver seems to be the site of the greatest initial withdrawal of vitamin B."

Using the chick as test animal, Keenan, Kline, Elvehjem, and Hart<sup>142</sup> find that the thermolability of vitamin B<sub>4</sub> is similar to that of vitamin B<sub>1</sub>; and that under some conditions of dry heat to which vitamin B<sub>1</sub> is relatively stable, vitamin B<sub>2</sub> may be inactivated.

Bisbey and Sherman<sup>143</sup> have studied the extractabilities and stabilities of vitamins B (B<sub>1</sub>) and G (lactoflavin) in the forms in which these occur naturally as in milk. An effective method for the complete extraction of all of the vitamin B complex from yeast has been described by Itter, Orent, and McCollum.<sup>144</sup> These workers<sup>145</sup> have also reported a simplified procedure for preparing lactoflavin, and a study of its growth effect. Stare<sup>146</sup> has described the preparation of hepatoflavin, and has found with this, as others have found with lactoflavin, that flavin is a growth-essential, but does not possess the entire growth-promoting or antidermatitic function of the heat-stable part of the vitamin B complex.

Lepkovsky, Popper, and Evans<sup>147</sup> have described the preparation of crystalline flavin (vitamin G) which, under their experimental conditions, promoted the growth of chicks; but which, in the hands of Lepkovsky and Jukes,<sup>148</sup> did not prevent the appearance of the so-called pellagra-like syndrome in chicks as also reported by Elvehjem and Koehn.<sup>149</sup> In view of the experiments of Booher,<sup>150</sup> as well as of several investigators abroad, it should not be inferred that promotion of growth and protection from skin troubles are functions of separate vitamins, but rather that of these two vitamins (G; and H, B<sub>6</sub> or Y) *both* are needed for permanently good skin condition as well as for growth.

A possible rôle of the sulfhydryl group in the syndrome usually viewed as vitamin G-deficiency was emphasized by Itter, Orent, and McCollum,<sup>151</sup> who found that certain sulfhydryl compounds cured the alopecia and tended to prevent a decline in weight in animals on a vitamin G-deficient diet; whereas, under the same conditions, lactoflavin failed to cause growth of hair but induced a definite gain in body weight.

Spies and Dowling<sup>152</sup> report the experimental production of anemia in dogs by means of a blacktongue-producing diet consisting of: cornmeal, 400 gm.; cowpeas, 50 gm.; purified casein, 95 gm.; cottonseed oil, 30 cc.; cod liver oil, 15 cc.; and salt mixture, 22 gm. They conclude that "in view of our present inadequate information concerning the nature of the chemical substance or substances involved, it seems unwise to assume that the dermatitis, stomatitis, anemia, neuritis, and dementia of pellagra in human beings; and the dermatitis, blacktongue, diarrhea, anemia, and neurological involvement developed in dogs restricted to an unbalanced diet are all produced by the lack of the same specific chemical substance."



According to Elvehjem, Sherman, and Arnold,<sup>153</sup> pork muscle, heart muscle, and kidney are "fairly rich" in vitamin B, whereas beef muscle, mutton muscle, brain, and lung are "very low." Sebrell, Wheeler, and Hunt<sup>154</sup> find rabbit meat, lean pork shoulder, and canned chicken to be good, peaches fair, prunes and canned beets poor sources of the pellagra-preventing substance. Morgan and coworkers<sup>155, 156</sup> have compared the quantitative distribution of vitamins B and G in wheat products and some other foods, and have found no significant loss of vitamin B in the baking of bread. Poe and Gambill<sup>157</sup> found an average of 0.21 unit of vitamin G value per cc. of home-canned tomato juice.

**Vitamin C.** The American Medical Association<sup>158</sup> has announced that, "By reason of its rules against therapeutically suggestive names, the Council could not recognize the name 'Ascorbic Acid,' although this term has been used in the literature. . . . The Council adopted the term 'Cevitamic Acid' as a non-proprietary designation for the crystalline vitamin C introduced as Ascorbic Acid. . . . The Council feels strongly that investigators in naming newly discovered medicinal substances should bear in mind the fundamentally sound objections to the use of therapeutically suggestive names."

Guerrant, Rasmussen, and Dutcher<sup>159</sup> have found that titration against a standard solution of 2,6-dichlorophenol indophenol yields results in satisfactory agreement with feeding experiments in the examination of grapefruit, lemon, orange, or fresh pineapple juice; but that "some juices contain interfering substances that react with the dye, thus complicating the titration results and leading to erroneous conclusions."

Dann and Cowgill<sup>160</sup> have reported results which indicate that the vitamin C requirement of the guinea pig is directly proportional to the body weight, and is almost exactly 1 cc. of lemon juice per 100 grams. "There is no evidence from these data that the young, rapidly growing guinea pig requires a proportionately greater amount of this dietary factor than the adult." They also conclude that: "The rôle of the metabolic rate, which in the case of vitamin B has been found to be of equal importance to body weight as a determinant of the requirement of various species for the vitamin, appears insignificantly small so far as vitamin C is concerned." These findings have a twofold significance for food chemistry in that, (1) they show the importance of vitamin C in practical food values for adults, and (2) they correct a very prevalent overestimate of the vitamin C value of lemon juice in terms of nutritional need. Goettsch<sup>161</sup> has compared the effects of pure vitamin C with those of orange juice in clinical scurvy of infants.

King and Menten<sup>162</sup> find that a liberal intake of vitamin C is favorable to stamina and ability to resist injury from diphtheria toxin.

Bogart and Hughes<sup>163</sup> have investigated anew the development of vitamin C in the sprouting of grain (in this case oats).

**Vitamin D.** The trend of recent work is strongly to complicate the consideration of vitamin D. Most students of the subject now recognize the existence of at least three vitamins D; while Bills, at the Johns Hopkins Conference on the Chemistry of the Vitamins (July, 1935), spoke of the probability of at least five.

Study of the species differences in the relative response to vitamin D from various sources, which earlier demonstrated the non-identity of the antirachitic factor in irradiated ergosterol with that in fish liver oils, and suggested the existence of at least two forms of the vitamin in the latter source, has now afforded abundant confirmation<sup>164-166</sup> of the finding of Waddell that the provitamin D in crude cholesterol is not ergosterol, and, indeed, it now appears probable that the light-activatable substance in animal tissues is not ergosterol<sup>166</sup>; on the other hand, plants of both higher and lower botanical orders contain a provitamin D which, like ergosterol, gives rise to an antirachitic factor relatively much less effective in the chick than in the rat.<sup>166</sup>

Carrying the vitamins D which are relatively less effective in the chick than in the rat are irradiated ergosterol, irradiated plant materials<sup>166</sup> (cottonseed oil, wheat middlings, alfalfa leaf meal, dried mycelium, yeast), and milk produced by cows fed irradiated yeast.<sup>165-168</sup> Containing the forms of vitamin D which are of relatively high effectiveness for the chick are cod liver oil, irradiated crude cholesterol,<sup>164-166</sup> irradiated animal products in general<sup>166</sup> (hog brains, butter fat, lard), irradiated milk,<sup>165, 168</sup> irradiated purified cholesterol in which activatability has been produced by heating,<sup>165, 169</sup> and apparently the cholesterolene sulfonic acid of Yoder.<sup>170</sup>

Clinical studies of the year lend increasing confidence to the assumption that antirachitic effectiveness as determined on the rat is a reliable measure of the potency in infantile rickets. Equal antirachitic effectiveness (rat unit for rat unit) in the human infant has been found for the various forms of "vitamin D milks": irradiated (fresh and evaporated), "fortified" (by the addition of cod liver oil concentrate), and "metabolized" (produced by cows receiving irradiated yeast).<sup>168, 171-174</sup> However, Compere, Porter, and Roberts<sup>175</sup> still find that 1.1 to 3.3 times as many rat units in the form of irradiated yeast as in the form of cod liver oil must be administered for comparable degrees of healing in human rickets.

The methods of increasing the vitamin D potency of dairy products have been discussed critically by Krauss and Bethke.<sup>176</sup> Guerrant and coworkers<sup>177</sup> and Russell and Taylor<sup>178</sup> have investigated further the relationship between the vitamin D intake of the hen and the antirachitic potency of the eggs produced. The Committee on Foods of the American Medical Association has disapproved fortification of "foods other than dietary staples" and of miscellaneous accessories with vitamin D.

Bills and his coworkers<sup>179</sup> reported a taxonomic study of the dis-

tribution of vitamins A and D in 100 species of fish, representing seventeen zoological orders. They found that three-quarters of the liver oils which they investigated were more potent than cod liver oil.

Vitamin D, however defined, appears a somewhat less controlling factor in rickets than has commonly been assumed during the preceding decade. In a paper on the phytin phosphorus of the corn component of a rachitogenic diet, Harris and Bunker<sup>180</sup> report the development of diets "which were devoid of extractable vitamin D, low in total phosphorus, and with Ca:P ratios as exaggerated as 8:1 (and which) failed to induce rickets" in rats. Healing of rachitic lesions in young rats transferred to a diet of normal phosphorus content but containing only traces of calcium and vitamin D has been reported by Jones and Cohn.<sup>181</sup> Huffman and Duncan<sup>182</sup> observed that rickets in calves on a diet inadequate in vitamin D may be checked by the addition of magnesium salts, although in the complete absence of vitamin D these salts are ineffective. Further observations on the alleged rachitogenic factor in cereals have been reported by Harris and Bunker<sup>180</sup> and by Lachat and Palmer.<sup>183</sup>

Evidence as to the effectiveness of vitamin D, or any of the five (?) vitamins D, in promoting *retention*, as distinguished from *mobilization*, of calcium and phosphorus in nutrition continues to be indecisive. Coons and Coons<sup>184</sup> find only slight and irregular effects under conditions of pregnancy with calcium and phosphorus need such as would seem to have been well suited to permit the vitamin to show whatever favorable effect it may have upon the economy of these elements in metabolism. Swanson and Iob<sup>185</sup> report that feeding vitamin D in the form of cod liver oil to the mother rat increased the calcium content of the offspring 10 percent, and their phosphorus content 12 percent. Slightly smaller increases resulted from the feeding of viosterol (commercial irradiated ergosterol), even though the dosage in antirachitic units was much more liberal.

Wallis, Palmer, and Gullickson<sup>186</sup> find that under certain conditions vitamin D is specifically needed by calves, and when given acts to improve the retentions of calcium and phosphorus as demonstrated by the balance of intake and output of these elements.

An extension of the studies on the interrelationship of the parathyroid hormone and vitamin D has led Morgan and Samisch<sup>187</sup> and also Jones<sup>188</sup> to the conclusion that vitamin D does not act exclusively through the parathyroid mechanism.

**Vitamin E.** According to press dispatches, Evans<sup>189</sup> has isolated vitamin E in crystalline form in sufficient quantities for identification. Olcott<sup>190</sup> has investigated further the chemical behavior of vitamin E; and Barnum<sup>191</sup> has studied the vitamin E content of eggs as related to the diet and to hatchability.

**Indications of Other Factors.** Leucopenia and anemia, resulting in the monkey from a vitamin deficiency or deficiencies the exact nature of which is still under investigation, have been reported by

Day, Langston, and Shukers.<sup>192</sup> Dried brewers' yeast prevented this deficiency disease. Almquist and Stokstad<sup>193</sup> report preliminary investigations of the apparent dietary origin of a hemorrhagic disease of chicks.

**Meats, Fish and Shellfish.** Pittman and coworkers<sup>194, 195</sup> have reported the second and third parts of their experimental investigation of the utilization of meat (here beef muscle, heart, and liver) by human subjects. Further studies upon the nutritive value of beef heart, kidney, round, and liver after heating and after alcohol extraction have been reported by Seegers and Mattill.<sup>196</sup> Williams and coworkers<sup>197</sup> continue their experiments upon the cooking of meats with acid to bring more of the calcium of meat-bone into the service of human nutrition.

Devaney and Munsell<sup>198</sup> find between 0.4 and 0.5 International unit of vitamin D per gram of beef or hog liver; slightly less than 0.2 unit in lamb liver; and only about 0.1 unit in calf liver. Oysters have been found by Whipple<sup>199</sup> to be "an excellent food source of vitamin B (B<sub>1</sub>), a relatively good one of vitamin A, and a very modest source of vitamin D." Devaney and Putney<sup>200</sup> find canned salmon a good source of vitamin D, and a variable source of vitamin A, of which one sample showed 30 times as much as another. The chemical and physical properties of haddock-liver oil, and its vitamin values, have been investigated by Pottinger and coworkers.<sup>201</sup>

Fowler and Bazin<sup>202</sup> have published the maxima, minima, and averages of their analyses of meats and fish for moisture, protein, fat and ash.

Coulson, Remington, and Lynch<sup>203</sup> find that the naturally occurring arsenic in the shrimp is in a form which, when the shrimp is eaten and digested, is rapidly eliminated through the kidneys and apparently without toxic effect.

Rupp<sup>204</sup> has investigated the effect of pH on the formation of ferrous sulfide from the viewpoint of preventing discoloration of canned meats. The chemistry of the deterioration of fish, and its prevention by carbon dioxide, have been studied by Stansby and Griffiths.<sup>205</sup>

**Eggs.** Bailey<sup>206</sup> has introduced a new method for the determination of the foaming power of egg white and for testing the stability of the foam. Unfrozen whites and whites thawed after short periods of frozen storage showed little if any difference in this property. Thick white, however, had a higher foaming power than thin white; and the stability of the foam was found to be influenced by various treatments. The addition of olive oil decreased foaming power to a greater extent than did the addition of the same amount of fat in the form of egg yolk. The same author<sup>207</sup> also shows the practicability of refractometric estimation of the total solids of eggs (white and yolk) and of egg-yolk magma. Sell, Olsen and Kremers<sup>208</sup> have studied lecithoprotein as the emulsifying ingredient of egg yolk and with

reference to mayonnaise. Preliminary results of an investigation of the gelation of egg sols in the presence of electrolytes have been reported by Woodruff, Pickens, and Smith.<sup>209</sup>

The transmission of light through egg shell as a factor in the candling of eggs has been studied by Givens, Almquist, and Stokstad.<sup>210</sup>

The nutritive value of the egg in child feeding has been investigated experimentally by Rose and Borgeson.<sup>211</sup> Devaney, Titus, and Nestler<sup>212</sup> find that feeding of vitamin D does not influence transfer of vitamin A to the egg; but considerable increases of vitamin A intake led to marked increases in the vitamin A values of the eggs produced. Koenig, Kramer, and Payne<sup>213</sup> have studied the vitamin A values of eggs as related to the laying-record of the hen. Young hens, nearing the end of their first four months of egg production, yielded eggs with yolks of similar value, about 25 units per gram; while near the end of a year of laying, those of low production laid eggs whose yolks showed 33 units, and those of high production, about 20 units. Pale eggs produced on a ration devoid of carotene and xanthophyll but containing cod liver oil had 25 units per gram of vitamin A value in the yolk.

**Milk.** Homogenization has been found by Trout, Halloran, and Gould<sup>214</sup> to increase the titrable acidity of raw, but not of pasteurized, milk. Also the process seemed to increase the viscosity of raw milk and to decrease that of pasteurized milk, though causing no important change in the specific gravity. The stability of the protein of milk toward alcohol was decreased by the homogenization, as was also the curd tension. Lasby and Palmer<sup>215</sup> have reinvestigated the effect of pasteurization and find no change in the calcium and phosphorus contents of milk, and no significant difference between raw and pasteurized milk as to the retention of these elements and the support of normal development of the bones. The nitrogen also was of equal nutritive value in raw and pasteurized milk.

The *phospholipids* of milk have been found by Perlman<sup>216</sup> to be more thermostable than previously supposed. He reports<sup>217</sup> that they are concentrated proportionately to the fat in cream up to a fat content of about 55-58 percent, beyond which the proportion of phosphatide diminishes.

Development of *color* in heated lactose solutions and evaporated milk has been studied by Webb.<sup>218</sup>

In the experiments of Jack and Bechdel,<sup>219</sup> the injection of thyroxine seemed to increase the yield but not to influence the composition of milk.

**Butter and Buttermilk.** Templeton and Sommer<sup>220</sup> report that the addition of citric acid or sodium citrate to either cream or the starter or both tended to produce a butter of superior flavor and aroma. Michaelian and Hammer<sup>221</sup> find that acetylmethylcarbinol and biacetyl are formed in the butter-making process, and have studied the conditions influencing their production. Whittier and Trimble<sup>222</sup> have investigated the differences in lactic acid content among butters. The

nature of the fatty materials in buttermilk has been further investigated by Bird, Breazeale, and Sands.<sup>223</sup>

**Cheese and Whey.** Goss, Nielsen, and Mortensen<sup>224</sup> have developed, at the Iowa Agricultural Experiment Station at Ames, a process for the manufacture and curing of a Roquefort-type cheese to which they have given the name Iowa Blue. Lane and Hammer<sup>225</sup> have investigated the effects of pasteurizing the milk used in cheese-making upon the transformations which occur in the nitrogenous constituents of Cheddar cheese. Heiman<sup>226</sup> finds that much the larger part of the vitamin G of milk passes into the whey in cheese-making, the whey solids showing about 50 percent higher vitamin G value than the solids of skimmed milk.

**Grain Products, Baking and Brewing.** Alsberg<sup>227</sup> has reinvestigated the variations in quality and baking value of wheat flours, with special reference to the influence of their starches. The diastatic activity of wheat as influenced by various factors has been studied by Swanson<sup>228</sup>; that of flour by Steller, Markley and Bailey<sup>229</sup>; and the catalase activity of wheat flour by Blish and Bode.<sup>230</sup> Bailey and Sherwood<sup>231</sup> have investigated the interlocking significances of the actions of amylases and of yeast in the breadmaking process.

Bayfield<sup>232</sup> has continued the study of the relations of the kinds and amounts of the proteins in wheats to the bread-making qualities of their flours. The effects of mixing and fermentation upon the protein structure and colloidal properties of dough, and the problem of free and bound water in bread doughs have been discussed by Skovholt and Bailey<sup>233</sup>; and the peptization of wheat-flour proteins under the influence of organic acids by Mangels and Martin.<sup>234</sup> Balls and Hale<sup>235</sup> have investigated the phenomena of proteolysis in flours.

The pigments of wheat have been studied extensively by Markley and Bailey,<sup>236</sup> and the bleaching of flour by Munsey.<sup>237</sup>

Hooft and de Leeuw<sup>238</sup> find acetylmethylcarbinol, formed as a by-product of the action of yeast upon sugar, in bread, where they believe it to be an important factor in flavor.

The distribution of nitrogen in the maize kernel at different stages of maturity has been reported by Zeleny.<sup>239</sup>

Bailey, Capen, and LeClerc<sup>240</sup> have reported their extended investigation of the composition and characteristics of soybeans, soybean flour, and soybean bread.

A notable symposium on developments in brewing processes and their control includes the papers of Schwartz,<sup>241</sup> of Michaelis,<sup>242</sup> and of Siebel and Singruen.<sup>243</sup>

**Fruits and Vegetables and their Products.** Haas and Klotz<sup>244</sup> have studied the solids, individual mineral elements, and pH of citrus fruits from the viewpoint of the influence of maturity and of the determination of physiological gradients between the calyx and styler halves of the fruit; and Haas and Bliss<sup>245</sup> have made a similarly thorough investigation of the composition of Deglet Noor *dates* in relation to water

injury. The composition of the developing *asparagus* shoot was studied by Culpepper and Moon<sup>246</sup> in relation to its use as food and its properties as material for canning. Total nitrogen showed its highest concentration at the tip, while the concentration of sugar was highest at the base and diminished toward the tip at all stages of growth. Adams and Chatfield<sup>247</sup> have published a new classification of fruits and vegetables according to their carbohydrate content.

Coleman and Ruprecht<sup>248</sup> found no marked or constant influence of soil type upon the mineral composition of vegetables; and concluded also that fertilizers containing nitrogen, phosphates, and potassium salts, when used in amounts necessary for optimal crop production, exert very little influence upon the composition of the vegetables grown with them. Haas<sup>249</sup> has reported upon the differences in chemical composition of the juices of *oranges* grown upon differently fertilized soil. Mitchell<sup>250</sup> has studied the relationships and variations of composition and color in commercial *tomato juice*. The Federal requirement for drained solids in *canned tomatoes* has been increased to 50 percent.<sup>251</sup> Pitman<sup>252</sup> finds the oil content to be the best criterion of maturity in *olives*.

Balls and Hale<sup>253</sup> have investigated the rôle of peroxidase in the darkening of the cut surfaces of *apples*, which is prevented by glutathione or cysteine salts. The respiratory activities and other chemical changes of apples in storage have been studied by Harding.<sup>254</sup> Advances in the technology of the production of apple juices, concentrates, and syrups are reported by Poore.<sup>255</sup> Baker and Kneeland<sup>256</sup> have investigated conditions for the extraction of *pectin* and control of the process by the determination of viscosity; they<sup>257</sup> have also studied the influence of diastatic preparations upon the properties of apple pectin.

Fellers and coworkers<sup>258</sup> have continued their investigation of *cranberries*. Joslyn and Marsh<sup>259</sup> have found that the browning of *orange juice* can be prevented by the addition of small amounts of sulfites or other antioxidants, or by canning the juice in tin.

Rittinger, Dembo, and Torrey<sup>260</sup> report favorably upon the use of *soybean* "milk" in feeding children. A soybean product containing lecithin and associated phosphatides with oil, and intended as an emulsifying agent for use in foods, has been "accepted" by the American Medical Association.<sup>261</sup> Horvath<sup>262</sup> shows the presence of at least two phosphatides in the soybean; and Jamieson and McKinney<sup>263</sup> find that, in general, soybeans of the western states are richer in phosphatides than those of the eastern states. Horvath<sup>264</sup> has contributed further to the chemical technology of the soybean industry.

Culp and Copenhagen<sup>265</sup> have studied the losses of iron, copper, and manganese from vegetables cooked by different methods.

Morgan<sup>266</sup> has reported her studies upon the influence of the customary dipping in lye, of air- and sun-drying, and of sulfuring, upon the vitamin values of fruits. Sulfuring, while conserving the vitamin C value, proved destructive of vitamin B (B<sub>1</sub>). With Hunt and Squier,<sup>267</sup>

she has determined the vitamin B and G values of *prunes*; dried California (French) prune flesh showed at least 2.66 units of vitamin G per gram, a value comparable with that which they obtained for wheat germ, whereas the wheat germ showed about ten-fold higher concentration of vitamin B than did the prune flesh. Morgan and her associates have also reported the vitamin values of *figs*,<sup>268</sup> and of *grapes* and *raisins*.<sup>269</sup>

*Grapefruit* was found by Roehm<sup>270</sup> to be an excellent source of vitamin G, though not of vitamin B. Both the leaf and the flower of *broccoli* were rich in vitamin G, though they contained only the moderate amounts of vitamin B which are found in green foods generally.

Batchelder and coworkers<sup>271</sup> find the *blackberry* to have a vitamin A value comparable with those of bananas, cantaloupes, and dates; and to be a relatively less potent, but not insignificant, source of vitamin C. Magistad<sup>272</sup> reports that the flesh of the *pineapple* owes its yellow color to both carotene and xanthophyll, the carotene predominating. The concentration of carotene ranged between 0.15 and 0.25 mg. per 100 grams of the pineapple flesh.

MacLeod and coworkers<sup>273</sup> studying the vitamin A values of five varieties of *sweet potato* found the Triumph and Southern Queen to show 2 and 4 units per gram, respectively, while the Yellow Jersey, Nancy Hall, and Puerto Rico varieties (all more highly pigmented) showed about 30 to 40 units per gram. Apparently the development of the provitamin A continued after the harvesting of the roots, as the vitamin A values were higher in the roots taken from storage than in those of the same variety freshly dug.

Fellers, Clague, and Isham<sup>274</sup> have compared the values of commercially canned and laboratory-prepared *tomato juices* as antiscorbutics. This work is deemed to show "that although individual samples of commercially or home-canned tomato juices vary considerably in vitamin C content, all may be considered satisfactory antiscorbutics." Somers and Sweetman<sup>275</sup> report relatively large differences in the antiscorbutic values of commercial tomato juice cocktails.

Kleiner and Tauber<sup>276</sup> find (by the oxidation-reduction titration method) much less vitamin C in *dandelions* than in other common greens.

A symposium on the *chemistry and technology of wine*, published in November, contains papers on: vinification in California wineries;<sup>277</sup> manufacture of champagne and sparkling Burgundy;<sup>278</sup> metals in wineries;<sup>279</sup> effect of filter aids and filter materials on the composition of wine;<sup>280</sup> volatile acids of wine;<sup>281</sup> rate of precipitation of cream of tartar from wine;<sup>282</sup> and pasteurization of New York State wines.<sup>283</sup> Joslyn and Marsh<sup>284</sup> have also reported the effects of cold and freezing storage on the rate and extent of removal of cream of tartar from wine and on other changes in its composition.

**Commercial Sweets.** During the year, Horne<sup>285</sup> has given us a comprehensive and expert review of the sugar industries of the United



States with their current developments. However, a few additional reports may be noted briefly. The distribution of impurities in the crystals of white sugar has been studied by Keane, Ambler, and Byall.<sup>286</sup> They found over 50 percent of the ash, sulfates, chlorides, sodium, potassium, and nitrogen to be located in the outer 5 percent of the crystal; whereas, calcium, sulfites, and color were more uniformly distributed throughout the crystals. Sugar from which the outer layer of the crystal had been dissolved off was found superior for the making of barley candies.

The hygroscopicity of sugars and sugar mixtures has been studied by Dittmar<sup>287</sup> from the point of view of preventing bacterial deterioration of sugars in storage. The bacterial causation of ropiness in maple syrup has been investigated by Fabian and Buskirk.<sup>288</sup>

**Other Studies of Food in Relation to Growth, Health, and Length of Life.** Fellers<sup>289</sup> records a large number of quantitative determinations of vitamins C and D in foods which are commonly used in the feeding of children and concludes "that the modern choice of foods for infants and young children, from a vitamin viewpoint, is well founded"; while on the other hand the experiments of McCay, Crowell, and Maynard<sup>290</sup> with a diet very rich in protein and vitamins has been much quoted in support of the general idea that with such a diet growth may be "forced" beyond the rate which is optimal for later health and for length of life. A group of rats whose growth was retarded by restriction of food intake lived longer than a parallel group which had been allowed to eat the same diet *ad libitum*. Retardation of growth in this way seemed to retard sexual development also;<sup>291</sup> but as the animals were not mated, these experiments yielded no information as to the influence of the food restriction upon reproduction or upon the offspring.

Sherman and Campbell<sup>292, 86</sup> have continued their study of the relation of food to length of life, in experiments having a quite different point of departure and continued through successive generations. Starting with a dietary which (like the food of the majority of people) was nutritionally adequate but not optimal, it was found that an increase in the proportion of milk resulted in a better and also more uniform nutritional response.<sup>292</sup> The improvement was partly but not entirely due to increased intake of calcium.<sup>86</sup> The investigation is being continued. Mendel and Hubbell<sup>293</sup> find that the rate of growth of the rats of the breeding colony of the Connecticut Agricultural Experiment Station has been increasing for 25 years and that "the improved growth rate has been accompanied by superior reproductive performance." Hitherto we have been accustomed to hear that heredity furnishes the plan for the growth and development of each individual, while the factors of environment (largely the chemical factors of the nutritional intake) determine to what extent the potentialities of the plan are actually realized. Now, Todd<sup>294</sup> recasts the statement with the introduction of a highly significant modification. He writes: "The adult physical pattern is the outcome of growth along lines determined by

heredity but enhanced, dwarfed, warped, or mutilated in its expression by the influence of environment in the adventures of life." The recognition that our control of environment can enhance the potentialities conferred by heredity is highly important. And while Todd speaks only of the physical pattern, the American Medical Association has been told in its Presidential address <sup>205</sup> that science promises to those who will take advantage of the newer chemistry of nutrition, "greater vigor, increased longevity, and a higher level of cultural development."

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## Chapter XVII.

### Insecticides and Fungicides.

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During 1934 and 1935 organic insecticides received increased attention. New uses that were found for the rotenone-bearing plants, derris and cube, greatly stimulated their importation. In 1934 about 1,000,000 pounds of derris root and 500,000 pounds of cube root were imported into the United States, whereas a few years ago neither was commercially available. Dusts made by diluting these finely ground roots to a rotenone content of from 0.5 to 1 percent are the most effective insecticides known for combating cabbage worms and the Mexican bean beetle, and leave no poisonous residues.

Chemists have been active in developing synthetic organic compounds as insecticides and fungicides. Phenothiazine is a striking example of this class. It is even more toxic than rotenone to mosquito larvae, killing them in a concentration of 1 part in 1,000,000. It has attracted much attention recently because of the promising results it has given against the codling moth. Phenothiazine is not toxic to warm-blooded animals when taken by mouth. Insecticide workers are now encouraged to believe that satisfactory substitutes for the poisonous arsenic, lead, and fluorine insecticides may be found among synthetic organic compounds.

**Arsenicals.** Richardson<sup>261</sup> tested arsenious oxide and acid lead arsenate in standard bran-molasses bait as poisons for the differential grasshopper. The median lethal dose of arsenious oxide is about 0.11 mg. per gram of body weight; that of acid lead arsenate is 2 to 4 mg. per gram. Whitehead<sup>338</sup> reported that bran poisoned with arsenic for grasshopper bait had no effect on quail or chickens. Gross and Nelson<sup>127</sup> described an apparatus for the determination of arsenic evolved from tobacco during smoking. To produce an insecticide, Thordarson<sup>319</sup> mixes neutral waste sulfite liquor and a solution containing arsenic and an alkali hydroxide and adds a soluble non-alkali metal salt to produce a precipitate. Dearborn<sup>69</sup> prepared homologs of Paris green in which formic, propionic, butyric, monochloroacetic, and trichloroacetic acids were substituted for acetic acid. Analysis indicated that these homologs, like Paris green, are definite compounds of copper meta-arsenite and the copper salt of the corresponding

acid and that the ratio of the two constituents is very close to 3:1 in all cases. Munday<sup>233</sup> produced a larvicide by agitating Paris green with a solution of sodium amyl xanthate, filtering, drying the powder, and sifting it. Latimer<sup>190</sup> makes arsenic acid by the action of iodine and nitric acid on arsenious acid, and Boller<sup>22</sup> oxidizes arsenious acid by air in the presence of an iodide and activated carbon. Wagner and Mowe<sup>327</sup> produce sodium pyroarsenate from arsenious oxide, sodium nitrate, and sodium carbonate. Tucker<sup>323</sup> reported that standard, or acid, lead arsenates burn foliage severely in the coastal fog belts of California, an effect that may be due to the reaction of the acid lead arsenate with sodium chloride carried from the ocean by winds, forming a basic chloroarsenate and releasing 35 percent of the original arsenic. A basic lead arsenate may be used in these regions without foliage injury. Various agents for increasing and maintaining lead arsenate deposits for codling moth control are discussed by Marshall, Edie, and Priest,<sup>203</sup> and the distribution of arsenic on the foliage of trees sprayed with arsenicals is discussed by Farley.<sup>87</sup> Kadow and Anderson<sup>178</sup> found that the addition of zinc sulfate to lead arsenate-lime sprays for peach trees prevented arsenic injury, and Poole<sup>250</sup> found that zinc sulfate and powdered sulfur are both effective in reducing the arsenical injury of peach trees treated with lead arsenate. Young<sup>350</sup> found that three or more thorough applications of herring oil-lead arsenate combination sprays reduced the carbon dioxide intake of apple leaves, and Hough<sup>160</sup> reported that severe foliage injury by lead arsenate occurred on trees sprayed heavily and frequently with oil during the previous season. The decrease in natural control of white-fly and scale insects by fungi on orange trees caused by the use of arsenical and copper insecticides was studied by Hill, Yothers, and Miller,<sup>155</sup> and the use of arsenical sprays reduced the percentage of parasitization by *Ascogaster carpocapsae* on codling moth larvae by more than one-half, according to Cox and Daniel.<sup>61</sup>

Hedenburg<sup>147</sup> manufactures zinc arsenate from zinc oxide, sodium hydroxide, and arsenic acid, and produces lead arsenate from litharge and arsenic acid in kerosene.<sup>148</sup> Dickson<sup>73</sup> has patented an insecticide comprising lead arsenate and ferric arsenate and also<sup>74</sup> an insecticide consisting of 85 parts of lead arsenate, 5 parts of lead cyanide, and 10 parts of Bordeaux mixture containing  $\frac{1}{4}$  copper.

The preparation of a new chloroarsenate of calcium,  $(\text{CaCl})_2 \cdot \text{HAsO}_4 \cdot 2\text{H}_2\text{O}$ , was reported by Smith.<sup>296</sup> Pearce, Norton, and Chapman<sup>246</sup> described a new method for determining the relative safeness to foliage of calcium arsenates, which is based on the observation that if water-soluble arsenic is determined after neutralization or removal of the free lime normally occurring in commercial preparations, values are obtained which may be used as an index to injury. Hagood<sup>133</sup> patented a method of preparing stabilized calcium arsenate insecticides containing a fluorine compound, and Fales<sup>86</sup> patented a plant-protecting agent containing calcium arsenate, basic copper sulfate, and nicotine.



Howard and Davidson<sup>163</sup> made six samples of calcium arsenate safe for use on bean foliage by treatment in an autoclave under 150 pounds steam pressure (366° F.) for two hours and subsequent drying at 131° F. for 48 hours. Marshall<sup>202</sup> reported that in an arid area the injury to foliage by calcium arsenate is eliminated by the use of a metal sulfate as a buffer; for example, 1 pound of zinc sulfate pentahydrate and 2 pounds of hydrated lime are added to 3 pounds of calcium arsenate per 100 gallons. Chapman<sup>49</sup> reported that calcium arsenate is perhaps equal to lead arsenate in toxicity to the apple maggot but is inferior against the codling moth in New York. Webster<sup>332</sup> reported that encouraging results have been obtained where calcium arsenate has been used with metallic sulfates and hydrated lime to check injury to foliage. Acid washes were effective in reducing the calcium arsenate deposit on apples. Webster<sup>333</sup> studied the arsenic deposit produced and the degree of codling moth control obtained by the use of lead arsenate, manganese arsenate, and calcium arsenate combinations with fish oil, calcium arsenate-mineral oil, and calcium arsenate soap.

**Antimony.** Burdette<sup>37</sup> reported that, when a spray containing an invert sugar syrup and 1.5 to 2 pounds of tartar emetic per 50 gallons was used on corn in the field, from 85 to 90 percent of the corn ear worm moths fed on the syrup but the toxic action was not sufficiently rapid to prevent egg laying before the moths died.

**Copper.** Collaborative studies on methods for the determination of copper and lead oxide in insecticides were reported by Graham.<sup>122</sup> de Ong<sup>240</sup> found it possible to carry minute amounts of copper into the tissue of leaves and twigs by the use of copper resinate dissolved in a specially prepared pine-tar oil, and later<sup>242</sup> reported that analysis of twigs 30 days after spraying with oil-soluble copper showed 60 percent of the copper originally applied on the surface and 21 percent in the tissue itself. No copper was found in the tissue of Bordeaux-sprayed twigs. Hildebrand and Phillips<sup>154</sup> found that, while copper sulfate is poisonous to bees, it is also a repellent and it is impossible to predict the damage to bees which might result from the application of copper sulfate to open fruit blossoms. Wilson<sup>343</sup> reported that the efficiency of Bordeaux mixture in controlling cucumber diseases was improved by the addition of one percent oil emulsion. Bordeaux mixture alone injured the plants. The best results were obtained with mixtures (sprays or dusts) of copper phosphate, copper sulfate, basic copper sulfate, basic copper chloride, or a copper ammonium silicate with calcium or manganese arsenate. Several patents on copper fungicides were issued. Green<sup>126</sup> patented copper silicate with lime, Sessions<sup>288</sup> a complex copper ammonium silicate, and Goldsworthy<sup>119</sup> copper phosphate with lime and also<sup>120</sup> cupric oxide with lime. Roberts and associates<sup>274</sup> reported good fungicidal results from the application of a copper phosphate-bentonite-lime spray, and Groves<sup>130</sup> reported control of apple scab with copper phosphate. A process for making a solution of copper and zinc sulfates, which comprises dissolving brass in dilute

sulfuric acid under pressure in the presence of compressed air, was patented by Corson,<sup>58</sup> who also <sup>59</sup> patented a process for producing copper sulfate by the action of sulfur dioxide and oxygen on copper in the presence of water. A process for impregnating the soil with an insoluble copper salt to combat termites was patented by Chandler.<sup>48</sup>

**Cadmium.** Migrdichian <sup>221</sup> patented a seed disinfectant comprising cadmium cyanide, cadmium diisopropyl dithiophosphate, cadmium cyanamide, cadmium xanthate, and cadmium phenyl cyanamide. Migrdichian and Horsfall <sup>222</sup> patented a seed disinfectant comprising a toxic metal salt of an aromatic hydrocarbon-substituted cyanamide, the toxic metal being selected from the group: lead, zinc, mercury, cadmium, bismuth, and iron.

**Zinc.** Kadow <sup>177</sup> reported that zinc sulfate-lime sprays were ineffective against peach scab, brown rot, and bacterial spot disease. Added to lead arsenate-lime sprays, zinc sulfate prevented rapid conversion of the lime into calcium carbonate and also prevented an increase in the concentration of water-soluble arsenic. Liipfert <sup>193</sup> patented a bactericide and fungicide composition comprising basic zinc sulfate intermixed with free calcium hydroxide in the form of a powder adapted to be dusted on plants and trees. Mills <sup>225</sup> patented aqueous solutions of zinc 2,4,5-trichlorophenolate as fungicides.

**Mercury.** Zimmerman and Crocker <sup>358</sup> reported that certain varieties of plants are injured by vapors from mercury or mercury compounds in the soil. There was evidence that mercury compounds in the soil are reduced to metallic mercury. Muncie and Frutchev <sup>232</sup> classified 25 fungicides tested for control of stinking smut caused by *Tilletia levis* on wheat in the following three groups: (a) certain organic mercurials, a mercury-copper carbonate mixture, two percent ethyl mercuric chloride, and copper carbonate, which were very effective; (b) mainly mercury-copper combinations, not yet sufficiently tested, which are promising; (c) calomel and other compounds, completely ineffective. Kharasch <sup>180</sup> patented a disinfectant in dust form for the control of seed and plant diseases, comprising an alkyl mercuric acetate and a dry diluting agent. Riker, Iranoff, and Kilmer <sup>265</sup> reported that mercuric chloride (1:1000) and cadmium chloride (1:100) are effective in killing all surface bacteria on nursery apple trees without visible evidence of root injury. Young <sup>356</sup> found that organic mercury dusts and formaldehyde controlled oat smut and the former exhibited stimulating effects on early-sown seeds. Dust containing ethyl mercuric chloride or phosphate improved the stand of cotton, although actual yield increases were few. A mercury ammonium silicate gel prepared by the action of a solution of mercuric chloride on a mixture of ammonium hydroxide and sodium silicate was used by White <sup>335</sup> as a treatment for gladiolus corms.

**Fluorine Compounds.** Sodium fluoride, pyrethrum, borax, and derris comprise the materials employed in roach powders, and the merits of various mixtures are discussed.<sup>4</sup> Fluoride-pyrethrum mix-

tures have come to be looked upon as the standard roach powder. Persing<sup>247</sup> reported that to increase the deposit and subsequent adherence of cryolite or barium fluosilicate when used with oil emulsions as fruit sprays, they should be wetted with the oil before being placed in the tank. The fluorine compounds, particularly natural cryolite, were found by Dobrosky<sup>79,1</sup> to be effective in the control of the tobacco flea beetle, the eggplant flea beetle, and the Mexican bean beetle. Dietz and Zeisert<sup>75</sup> found barium fluosilicate dusts to control black and margined blister beetles and to be safe to a comparatively wide range of plants. Basinger and Boyce<sup>18</sup> controlled the orange worm by dusting the trees in June-August with a mixture of barium fluosilicate, cryolite, fiber talc, and refined mineral oil or by spraying with cryolite. DeLong<sup>70</sup> concludes from a review of the literature that synthetic cryolite is superior to natural cryolite.

**Sulfur.** McGregor<sup>209, 210</sup> reported that the effectiveness of sulfur dusts against the citrus thrips is related to the percentage of sulfur that passes a 325-mesh sieve. Finely ground sulfur is effective against the smutty fungus of citrus. Tower and Dye<sup>322</sup> patented a parasiticide composition consisting of 100-mesh powdered sulfur coated with a substantially water-insoluble green dye and dye carrier to render it inconspicuous on foliage. The preparation of a colloidal bentonite-sulfur, much more toxic than mechanical mixtures, is described by McDaniel.<sup>207</sup> Davis and Young<sup>65</sup> found flowers of sulfur the best form to use for fumigation in a mushroom house; the distribution of the sulfur dioxide gas produced was studied. They<sup>67</sup> also determined the optimum gas concentration and time of exposure for various conditions of temperature and humidity for sulfur fumigation of mushroom houses, and described<sup>66</sup> the construction of an outside sulfur burner for mushroom-house fumigation. Henderson<sup>149</sup> found calcium sulfide alone, of all fungicides tested, to give results approaching commercial control of downy mildew of tobacco. The composition, properties, and uses of sulfur spray materials are discussed by Groves,<sup>129</sup> and the factors affecting the fungicidal value of lime-sulfur solutions and elemental sulfur by Peterson.<sup>249</sup> MacDaniels and Burrell<sup>199</sup> presented data confirming the view that sulfur applied as a dust or lime-sulfur spray, either before or shortly after pollination, reduces the set of apple fruit. The method of Kühl<sup>187,1</sup> is applied by Small<sup>295</sup> to the determination of the amount of sulfur adhering to the foliage of trees treated with sulfur fungicides. Hurt<sup>167</sup> patented a method for the preparation of an insecticide and fungicide comprising adding sulfonated water-gas creosote oil to a solution of calcium polysulfides. Christmann and Jayne<sup>50</sup> claim an insecticide comprising powdered sulfur, a wetting agent, and a deflocculating agent.

**Selenium.** Ries<sup>264</sup> reported that a proprietary insecticide containing selenium compounds showed promising results against eggs and active forms of a new mite (*Neotetranychus buxi*) on boxwood. Gnadinger<sup>114</sup> patented insecticides containing sodium, potassium, potassium-

ammonium, and sodium-ammonium selenosulfides, and also <sup>115</sup> an insecticide containing ammonium selenosulfide and a process for making this substance.

**Miscellaneous Inorganic Compounds.** McCallan and Wilcoxon <sup>208</sup> presented data on the toxicity to certain fungi and spores of compounds of the elements arranged in terms of the periodic system. The toxicity increases toward the center of the periodic table and is less at the two ends; toxicity within a group increases with molecular weight. Compounds of positive elements show nearly the same toxicity regardless of the compound used, but hydrides of negative elements are all toxic, while highly oxidized forms are only slightly so. Compounds of silver and osmium are the most toxic. Other elements besides mercury and copper that can be used as fungicides are cerium, cadmium, lead, thallium, chromium, and arsenic. Karns <sup>179</sup> patented a preparation for freeing plants of parasites, which consists of a mixture of an iodine compound (e.g., iodides of sodium, potassium, calcium, barium, etc.) and an oxidizing agent, which under atmospheric influence undergo reaction, slowly releasing free iodine. Hamilton <sup>140</sup> patented a jelly-like ant-killing mixture containing a thallium compound, sugar, water, agar, and honey. Exposing apples to a solution of sodium hypochlorite in the rinse water after the washing process is recommended by Baker and Heald <sup>15</sup> for the prevention of blue-mold decay.

**Spray Residue Removal.** The United States Department of Agriculture requires that fruits shall not bear more than 0.01 grain of arsenious oxide ( $\text{As}_2\text{O}_3$ ), 0.018 grain of lead (Pb), and 0.01 grain of fluorine (F) per pound when offered for interstate shipment. Much activity was manifested in 1934 and 1935 in devising analytical methods for determining, and methods and apparatus for washing off, spray residues on fruits. Wichmann, *et. al.* <sup>340</sup> described six methods for the determination of small quantities of lead, particularly in insecticidal spray residues, and Frear and Haley <sup>96</sup> proposed a method for the rapid determination of lead residues on apples, which is based on the use of the photronic cell. The solvent action on lead arsenate of a number of inorganic and organic acids, acids plus salts, salts, alkaline solutions, alkaline solutions plus salts, and wetting agents with and without acid was studied by Carter. <sup>44</sup> Addition of mineral oil to acid wash solutions reduces the danger of fruit injury at high temperatures and increases the efficiency of residue removal, according to Smith. <sup>299</sup> Beaumont and Haller <sup>19</sup> discussed the effectiveness of seven wetting agents in removing lead residues from apples. Horsfall and Jayne <sup>157</sup> reported that wool grease, thinned with petroleum naphtha, may be used to control excess foaming when Vatsol is used with certain washing compounds in commercial washing machines where agitation is present. The effect of the spray program adopted on the amount of lead residue on apples and its removal is discussed by Haller, Beaumont, Murray, and Cassil. <sup>138</sup> Haller, Smith, and Ryall <sup>139</sup> described the optimum conditions for removal of spray residues by hydrochloric acid and by

sodium silicate. The removal of arsenic residues by hydrochloric acid from apples receiving various spray schedules is discussed by McLean and Weber<sup>211</sup> Bordeaux residues on fruits and vegetables are removed by dilute acetic acid. Wakeland<sup>328</sup> summarized numerous data on the lead and arsenic contents of washed apples in relation to the spray program. Haller, Beaumont, Gross, and Rusk<sup>187</sup> gave general recommendations for washing apples with hydrochloric acid, with salt and a wetting agent if necessary, to remove lead arsenate. Fluke, Dunn, and Ritcher<sup>94</sup> reported that sodium silicate aids in the removal of lead arsenate spray residues from apples by three methods which differ from the usual tank washing: (1) By incorporation of the silicate in the last regular lead arsenate spray; (2) by applying a spray of silicate of soda, followed by clear water, to the fruit just before picking; and (3) by dipping the picked fruit first in an unheated bath of sodium silicate and then in an unheated water bath. Carter<sup>45, 46</sup> reported that sodium chloride, sodium bicarbonate, and monosodium phosphate each decreases the solubility of cryolite in water at 20° C. Boric acid, aluminum salts, and ferric salts increase the solubility of cryolite in 1.5 percent hydrochloric acid or water. The results of recent experiments on the removal of lead, arsenic, and fluorine residues from apples with various washes are discussed by Smith, *et. al.*<sup>300, 301</sup> Ryall<sup>279</sup> reported that a double washing process using sodium silicate or sodium carbonate, followed by hydrochloric acid, is more effective than either solution alone for the removal of fluorine residues. Mineral oil added to acid increases its effectiveness. Sodium chloride decreases the solvent action on fluorine, while ferric chloride and aluminum sulfate show promise for increasing the solvent action of hydrochloric acid. Fruit sprayed throughout the season with cryolite has not been consistently cleaned below the tolerance for fluorine by any method so far devised. McLean and Weber<sup>212</sup> patented a process for washing to remove spray residue with a solution containing 1 to 2 percent hydrochloric acid, 0.5 to 1 percent of a sulfonated aromatic hydrocarbon, and not over 0.5 percent of a substance to prevent foaming. A general view of the arsenic and lead spray residue situation throughout the country during 1933 was presented by White.<sup>336</sup> Henry<sup>150, 151</sup> patented processes for the removal of residual poisons from fruits and vegetables which comprised subjecting them to a dilute solution of hydrochloric acid or an alkali, with subsequent removal of the alkali by washing in water.

**Wetters, Spreaders, and Adhesives.** Hensill and Hoskins<sup>152</sup> proposed definitions for wetting agent, spreader, sticker, and emulsifying agent. Cupples<sup>64</sup> reported a study of the wetting and spreading properties of sodium hydroxide-oleic acid mixtures. Ginsburg<sup>109</sup> found several new sulfated fatty alcohols (10 to 18 carbon straight chain) and their sodium salts, sulfated fatty acids, and sulfated phenol compounds to have promising properties as spreaders. Cory and Langford<sup>60</sup> studied a number of sulfated alcohols to ascertain their value as toxic agents for insects, as emulsifying agents for oils and other

insecticides, as dispersing and carrying reagents for insecticides that deteriorate in alkaline solution, as wetting agents for alkaline and acid sprays, and as an aid in removal of the arsenical and lead residues on sprayed fruit. Bousquet<sup>24</sup> patented a contact insecticide comprising an aqueous preparation containing technical soybean lecithin as the essential active ingredient and sulfonated fish oil as a dispersing agent. Eddy<sup>84</sup> described two formulas for the preparation of a spreader for nicotine consisting of pine tar oil, in one formula plus water, potassium hydroxide, ethyleneglycol monoethyl ether, oleic acid, and in the other formula plus phenol and isoamyl alcohol. Littooy and Lindstaedt<sup>197</sup> patented a spreader for insecticidal use comprising a thorough mixture of lime, soybean flour, and skimmed-milk powder. Green<sup>125</sup> patented a flocculated bentonite, characterized by failure to swell or disperse in water, for use as an adjuvant for horticultural sprays. The preparation of a bentonite-Bordeaux mixture is described. Barnhill<sup>17</sup> patented a pest-annihilating dusting composition comprising a toxic ingredient (sulfur, cupric sulfate, hydrocyanic acid, Paris green, nicotine, etc.) and oil sorption foots (clay, fuller's earth, or bentonite that has been used to refine oils). Merrill<sup>214</sup> patented a process for the production of an insecticide by mixing a finely divided water-insoluble toxic compound (e.g., arsenious oxide, Paris green, London purple, or barium carbonate) in molten asphalt and emulsifying with a slurry of clay and water. Fulton<sup>99</sup> patented an insecticidal spray non-injurious to foliage comprising a finely divided gas black in colloidal suspension in a neutral aqueous liquid containing an emulsifying agent, e.g., soap. Yothers and Miller<sup>349</sup> found blood albumin to be an effective adhesive for sulfur dusts. Forbes<sup>95</sup> patented an insecticidal and fungicidal dusting powder comprising a hygroscopic mixture of desiccated milk and molasses and an active agent. Dills and Menusan<sup>76</sup> reported a study of the relative toxicity to insects of a number of fatty acids and their soaps. Fleming and Baker<sup>89</sup> reported laboratory tests with contact insecticides against Japanese beetles which showed that sodium soaps are more effective than potassium soaps, and soaps containing excess alkali are more effective than neutral soaps or soaps containing free oleic acid. The effectiveness of the neutral potassium soaps of the saturated fatty acids increases with the molecular weight. Eddy<sup>82</sup> described a preparation of soybean oil and meal suitable for emulsifying mineral oils for spraying. Flint and Salzberg<sup>91</sup> patented certain amino alcohol salts of organic acids (e.g., methylglucamine stearate) for use as emulsifying agents for insecticides.

**Oils and Emulsions.** Cressman and Dawsey<sup>62</sup> reported spraying experiments with mineral oil emulsions which showed that oil deposit and insecticidal efficiency vary inversely with the concentration of soap emulsifier in the aqueous phase and directly with the concentration of oil in the emulsions. Rohrbaugh<sup>275</sup> reported a study of the penetration and accumulation of petroleum spray oils in the leaves, twigs, and fruit of citrus trees. Young<sup>353</sup> described with the aid of drawings the

microscopic and macroscopic phenomena observed during the freezing and melting of Cresoap emulsions of six commercial petroleum oils. He<sup>354</sup> also demonstrated a general parallelism between the tolerance of fungi and of apple leaves to petroleum oils having less than 11 per cent of sulfonatable matter. A technic for predicting oil injury in apple is based on this phenomenon. Martin<sup>204</sup> discussed the employment and study of petroleum oil as a spray insecticide. The sulfonic acids produced during acid refinement include gamma-acids whose calcium salts are water-soluble and are promising spray materials, and beta-acids, the acids and the sodium salts of which are relatively oil-soluble and of possible use as emulsifiers. Carter<sup>47</sup> reported the successful use of Diesel fuel oils as insecticides when adequately emulsified and dispersed in water. Cleveland<sup>52</sup> found a new type of summer spray oils which exhibits distinctive physical properties in regard to spreading, oil deposit, thickness of film, and retardation of rate of penetration into fruit and leaf tissue, as compared with the usual type of cream emulsion or tank-mix oils, and are superior to the latter for codling moth control. Ebeling<sup>81</sup> made a comparative study of results obtained in control of red scale on lemon by treatment with three low-concentration oil sprays at intervals and with a single more concentrated spray. The former method gave very promising results. Farrar and Kelley<sup>88</sup> found that dormant oil sprays applied over 5- and 10-year periods to relatively young apple trees did not affect tree growth measurably under orchard conditions. Knight<sup>184</sup> reported that both glyceryl oleate and aluminum naphthenate improve the viscosity and persistence of petroleum oils and increase the insecticidal effectiveness against the codling moth and pear psylla. Freeborn, Regan, and Berry<sup>97</sup> studied the effect of petroleum-oil sprays in increasing the body temperature of dairy cows. Woglum and LaFollette<sup>345</sup> reported that soluble oils promise to displace pasty emulsions and tank-mix in citrus spraying. Young<sup>355</sup> found that decane caused ring-spot of apple leaves and killed juvenile apple leaves and dormant apple buds. Fifty percent of decane in a spray oil apparently did not increase the toxicity of the oil to apple leaves. Decane killed the treated parts of potato leaves and passed into the stems. It passed from onion leaves to the roots. Decane is present in petroleum oils, but in its pure form is too toxic to represent petroleum spray oils in experimental work. Stanley, Marcovitch, and Andes<sup>810</sup> reported that the control of the San Jose scale and peach leaf curl is in direct proportion to the amount of creosote oil (wood oil) in the spray. Mixtures of creosote oil and oil emulsion for control of these pests produce a synergistic effect. Parker, Shotwell, and Morton<sup>245</sup> reported that grasshopper baits containing a low-grade lubricating oil gave higher kills than non-oil baits containing molasses and water. Newcomer<sup>237</sup> has reviewed recent work on oil sprays as insecticides. Adams<sup>7</sup> patented a composition capable of forming a stable emulsion and intended as an antiparasitic spray for plants and trees, which consisted of oil-soluble mineral oil sulfonates,

soda resin soap, water, alcohol, straw oil, and creosote. Grant<sup>124</sup> patented an insecticidal composition comprising an oil-wax gel. Horne and Hopkins<sup>156</sup> patented a process for rendering a shale-oil distillate miscible with water. Volck<sup>324</sup> patented a method of applying parasiticidal oil to infested plants, which consisted in embracing the oil in finely divided dried cane sugar and then dusting the resultant powdery material upon the plant. Volck<sup>325</sup> also patented a parasiticidal spray comprising an emulsion of a non-volatile oil, water, and an ammonia soap of a fatty acid. Johnson<sup>171</sup> patented a spray for use against mealy bugs on pineapples, consisting of an emulsion of water, iron sulfate, clay, and refined mineral oil. de Ong and Smith<sup>243</sup> patented a process in which pine oil is oxidized by bubbling air through it and then neutralized, yielding a product safe to spray on plants and soluble in petroleum.

**Tar Distillates.** Hartzell, Harman, and Reed<sup>145</sup> found the use of mixtures of tar distillates and lubricating-oil emulsions objectionable because they appear more toxic to weak trees than either oil alone. They stressed the desirability of standardization of spray oils. Hartzell<sup>144</sup> and Hurt<sup>166</sup> discussed the physical and chemical properties and uses of tar-distillate sprays.

**Synthetic Organic Insecticides and Fungicides.** Oserkowsky<sup>244</sup> reported that exposure to saturated vapors of naphthalene or its monochloro or monobromo derivatives, trioxymethylene, benzene, toluene, xylene, nitrobenzene and *o*-, *m*-, and *p*-dichlorobenzene killed the mycelium of *Sclerotium rolszii*. Substitution of a nitro radical in the benzene ring resulted in greater toxicity than the substitution of amino, bromine, or two chlorine atoms in the para position. Substitution of bromine for chlorine in chloropicrin increased the toxicity. Ginsburg and Granett<sup>111</sup> tested 74 organic compounds against silk moth larvae, and found pentachlorophenol, cinchonine, nicotine tannate, and diphenylguanidine to be highly toxic and methoxyquinoline, diphenylguanidine, isoquinoline, and *o*-nitroanisole to be distinctly repellent.

Many patents have been issued covering the use as insecticides of a wide variety of organic compounds. Products patented include *o*-phenylphenol, by Britton and Mills<sup>31</sup>; *o*-phenylphenol emulsified in water with coconut oil soap, by Schaffer and Tilley<sup>285</sup>; a mixture of phenylphenols, by Britton<sup>30</sup>; a mixture of  $\alpha$ - and  $\beta$ -naphthols, by Britton and Stearns<sup>33</sup>; a mixture of phenol naphthenates in a petroleum hydrocarbon oil, by Teichmann<sup>317</sup>; chlorobenzene, by Seydel<sup>289</sup>; *o*-dichlorobenzene in solid solution in rubber, by Gardner<sup>101</sup>; an oil emulsion containing triamylamine, by Sharples<sup>291</sup>; the reaction product of a mono- or diamylamine with a dihalogenopentane, by Wilson<sup>344</sup>; compounds of hexamethylenetetramine with chromium, copper, or lead, by De Rewal<sup>72</sup>; and certain diazoamino compounds, by Markush.<sup>201</sup> Britton<sup>29</sup> patented a method for the preparation of sodium *p*-phenylphenate. Salzberg and Meigs<sup>282</sup> patented a parasiticide comprising an organic fluorine compound selected from the class consisting of fluoronaph-



thalenes, fluorodiphenyls, fluoroanilides, fluorophenols, fluoroacetic acid, and phenylfluoroform. Esters of benzoic and salicylic acids have been patented; for example, a mineral-oil solution of an alkyl benzoate (1 to 6 carbon alkyl groups), which may be combined with the oil-soluble principles of pyrethrum flowers, by Adams<sup>8</sup>; certain 5-alkylsalicylic acids as fungicides (e. g., 2-hydroxy-5-*sec*-amylbenzoic acid and 2-hydroxy-5-*sec*-hexylbenzoic acid), by Bruson and Stein<sup>84</sup>; and aralkyl esters of salicylic acid as insect repellents, by Cleveland.<sup>51</sup> Merrill<sup>215</sup> has patented a diethyleneglycol monoalkyl ether ester of meta-arsenious acid suitable for use as an insecticide and wood preservative. Knight and associates<sup>185-187</sup> have patented mixtures of mineral oil with various products, such as partially esterified glyceryl oleate and aluminum naphthenate, an oil-soluble ester of a fatty acid derived from an organic oil, and a polyhydroxy alcohol partly esterified with a high-molecular weight fatty acid. These mixtures are emulsified in water and sprayed on plants. Sibley<sup>293</sup> patented an insecticide comprising an alkali or alkaline-earth salt of a sulfuric acid derivative of the reaction product of a monohydric aliphatic alcohol containing less than 17 carbon atoms and a hydroxy-substituted diaryl containing 12 to 20 carbon atoms. Burwell<sup>38</sup> patented an insecticidal, bactericidal, and fungicidal composition comprising, in liquid dispersion, a mixture of alkali salts of saturated aliphatic monocarboxylic hydroxylated ketonically-constituted acid oxidation products of 4- to 15-carbon petroleum hydrocarbons, accompanied by non-acidic, unsaponifiable, generally ketonic, oxidized compounds of petroleum hydrocarbons. Sharma<sup>290</sup> patented a process in which fruit is coated with a waxy material containing a chloramine to retard decay from mold spores.

The organic sulfur compounds have been found to contain many insecticides and fungicides. Campbell, Sullivan, Smith, and Haller<sup>42</sup> reported that, of 68 synthetic organic compounds, most of which contained sulfur, 24 were found to equal or exceed nicotine in effectiveness against culicine mosquito larvae. Diphenylene oxide and diphenylene sulfide were the most effective. Of seven thioethers tested, phenylacetimido-thio-*p*-tolyl ether hydrochloride was the most toxic. Roark and Busbey<sup>272</sup> issued a comprehensive bibliography, with brief abstracts, of the literature relating to the use of organic sulfur compounds (exclusive of mothproofing materials) as insecticides. Hartzell and Wilcoxon<sup>143</sup> reported that, of various organic thiocyanogen compounds examined as insecticides, the most satisfactory was  $\gamma$ -thiocyanopropyl phenyl ether, which acted as a paralytic agent and was non-injurious to plants. Later Wilcoxon and Hartzell<sup>341</sup> reported that, of five organic thiocyanates tested as insecticides, only trimethylene dithiocyanate was equal to or better than  $\gamma$ -thiocyanopropylphenyl ether. Yeager, Hager, and Straley<sup>348</sup> found that 10 aliphatic thiocyanates tested tended to inhibit the contraction rate of the isolated heart preparation of the oriental roach. The thiocyanates produce increased heart dilation by causing an increased tonus of the alary muscles.

Bousquet, Salzberg, and Dietz<sup>25</sup> reported a study of the relation between molecular weight and toxicity to insects of the thiocyanates of the higher fatty alcohols. Patents have been issued to Lee<sup>191</sup> for a process of making *sec*- and *tert*- alkylthiocyanates, to Salzberg and Bousquet<sup>280</sup> on the use of lauryl thiocyanate against lower forms of life, to Alvord<sup>10</sup> for the use of thiazoles as a bactericide and fungicide, to Tisdale and Williams<sup>321</sup> for sodium dimethyl dithiocarbamate, and to Remy<sup>280</sup> for fuller's earth impregnated with readily vaporizable organic disulfides recoverable from petroleum. Neiswander<sup>234</sup> reported that a proprietary aliphatic thiocyanate was successfully used for the control of greenhouse mealybugs. Wilcoxon and McCallan<sup>342</sup> showed that the organic thiocyanates and the alkyl and acyl resorcinols are highly toxic to fungi. The thiazoles, catechol, and pyrocatechuic acid are less effective. Tests on control of tomato-leaf mold indicated that, while trimethylene dithiocyanate was equal to Bordeaux mixture and sulfur dust, none of these gave control of the disease. Salzberg and Bousquet<sup>281</sup> patented a parasiticide comprising a compound of the formula R-(CNX) in which R = an aliphatic hydrocarbon radical of at least 6 carbon atoms, X = sulfur, selenium, or tellurium, and the group CNX stands for the radicals thiocyano, isothiocyano, selenocyano, iso-selenocyano, tellurocyano, and isotellurocyano (e. g., lauryl, cetyl, stearyl, and octyl thiocyanates). Bolton<sup>23</sup> patented an insecticide comprising an organic substance containing in its molecule a 5-membered ring composed of 3 carbon, 1 sulfur, and 1 nitrogen atom, 1 of said carbon atoms carrying a salt-forming group. Smith, Munger, and Siegler<sup>302</sup> reported that phenothiazine shows promise as a substitute for lead arsenate in codling moth control.

**Cyanides.** Peters<sup>248</sup> described a new apparatus for measuring hydrogen cyanide concentration in tree fumigation, which draws the sample through a known volume of five percent potassium bicarbonate solution, after which the hydrocyanic acid is determined by titration with standard iodine solution. The results of studies on the effect of temperature and relative humidity on fumigation with hydrocyanic acid against red scale were reported by Quayle,<sup>256</sup> Quayle and Rohrbach<sup>258</sup> and Moore.<sup>228</sup> Pratt, Swain, and Eldred<sup>254</sup> found that of a large number of organic and inorganic gases tested as auxiliaries methylthiocyanate was the only one which increased the toxicity of hydrocyanic acid to scale insects, but this combination caused severe foliage injury. Haas<sup>131</sup> made a study of the chemical composition of citrus scale insects in relation to the part of the tree infested and also in relation to the resistance of the scale to cyanide fumigation. Quayle and Ebeling<sup>257</sup> reported that red scale resistant to hydrocyanic acid fumigation is controlled well by fumigating twice or by spraying with heavy oil to loosen the scales and then fumigating. Swain and Buckner<sup>312</sup> reported that the use of a form to hold the fumigating tent away from the citrus tree definitely increased the effectiveness of control of scale on the periphery of the tree, because the concentration of hydro-

cyanic acid is lower near the tent wall than near the center of the tree. Haas and Quayle<sup>132</sup> reported that, to avoid injury, fumigation with hydrocyanic acid should be delayed after copper treatment of citrus trees. Citrus trees showing damage from fumigation year after year contained relatively large amounts of copper. Bliss and Broadbent<sup>21</sup> made a statistical study of stupefaction time and mortality as criteria for the measurement of the action of hydrocyanic acid upon *Drosophila melanogaster* Meigen. Young, Wagner, and Cotton<sup>352</sup> reported that, for general purposes, a dosage of 8 ounces of hydrocyanic acid per 10,000 pounds of flour for a 3-hour exposure is effective against all stages of the flour beetle. This dosage is based on the use of low pressure (about 2 inches of mercury) and with flour temperatures of 70° F. or higher. Cupples<sup>63</sup> listed, with brief abstracts, all references appearing in the 1930 abstract journals concerning cyanide compounds used as insecticides.

Several patents covering the manufacture and application of cyanide compounds as fumigants were issued. Pranke<sup>251</sup> produces sodium cyanide from sodium calcium cyanide by treating the latter with liquid anhydrous ammonia. Carlisle and Dangelmajer<sup>43</sup> prepare hydrated calcium cyanide from unslaked lime and hydrocyanic acid. Macallum<sup>198</sup> prepares cyanide from formamide and sodium carbonate. Gilbert<sup>107</sup> produces alkali metal cyanide and calcium carbide from calcium cyanamide and alkali metal. Pranke<sup>252</sup> produces cyanide by reaction of a melt of calcium carbide, sodium chloride, and carbon with nitrogen. Marvin and Walker<sup>205</sup> produce hydrocyanic acid containing 0.05 to 0.5 percent of sulfur dioxide by the action of an acid on a mixture of sodium cyanide and a metal sulfite. Pranke<sup>253</sup> claims a process for the preparation of calcium sodium cyanide,  $\text{CaNa}_2(\text{CN})_4$ . Dunning,<sup>80</sup> and Magill, Dunning and Ressler<sup>200</sup> patented a process for the generation of hydrocyanic acid; Harris<sup>141</sup> prepares hydrocyanic acid from carbon, ammonia, hydrocarbon, and oxygen. Buchanan and Winner<sup>36</sup> patented a process in which a crude cyanide compound containing a cyanide unstable in aqueous solution is treated with water vapor under reduced pressure and hydrocyanic acid is recovered. Houghton<sup>161</sup> prepares a sealed package containing a mixture of carbon tetrachloride and acetone having hydrocyanic acid and cyanogen chloride absorbed therein. Cooper<sup>57</sup> patented a fumigant comprising a mass containing a water-decomposable cyanide and a hygroscopic soluble salt of an alkali-earth metal. O'Daniel<sup>238</sup> claims a method of fumigating grain with calcium cyanide.

**Ethylene Oxide.** Horsfall<sup>158</sup> reported that ethylene oxide affects the stage or portion of the bean weevil that is undergoing the greatest cellular activity. It is thought that the factors favoring an increased intake of oxygen also favor the intake of ethylene oxide. Britton, Nutting, and Petrie<sup>32</sup> patented a method for the preparation of ethylene oxide from chlorohydrin, and Baer,<sup>13</sup> a method of fumigation with carbon dioxide and ethylene oxide. Young and Busbey<sup>351</sup> published

a list of 189 references relating to the use of ethylene oxide for pest control.

**Chloropicrin.** Godfrey<sup>117, 118</sup> and associates found that adequate confinement of chloropicrin in the soil by means of an impervious cover is indispensable for nematode control. In the greenhouse, kraft paper, sized with casein glue and sealed down at the edges, was efficient, as was paper covered with cellulose acetate. Barnes and Fisher<sup>16</sup> studied the stimulating effect of chloropicrin, ethylene dichloride-carbon tetrachloride, carbon disulfide, and calcium cyanide on fig insects by determining the number of insects caused to leave the fruit before death occurred. Ramage<sup>259</sup> makes chloropicrin by chlorinating nitromethane in an acid solution. Johnson<sup>170</sup> reviewed the advantages of chloropicrin for fumigation, and Roark<sup>267</sup> and Roark and Busbey<sup>273</sup> prepared bibliographies of chloropicrin containing a total of 614 references.

**Miscellaneous Fumigants.** Shepard and Lindgren<sup>292</sup> found carbon disulfide to be more toxic than ethylene dichloride or propylene dichloride to the rice weevil, while for the confused flour beetle the relation is reversed, carbon disulfide being less toxic. It is therefore impossible to generalize regarding the relative toxicity of various fumigants. The respiratory response of adult *Orthoptera* to carbon dioxide, carbon disulfide, nicotine vapors, and hydrocyanic acid was studied by McGovran.<sup>208</sup> Zimmerman<sup>357</sup> determined the lowest concentration of gas necessary to cause anesthesia in centipedes, katydids, and rose chafers for propylene, butylene, ethylene, acetylene, carbon monoxide, and carbon dioxide. The anesthetic effect of these on plants and of carbon monoxide on *Mimosa pudica* was also studied. Jones<sup>176</sup> reported that the toxicity of a given concentration of carbon dioxide to the confused flour beetle may be markedly increased by the addition of small quantities of methyl formate. Klotz<sup>183</sup> found concentrations of nitrogen trichloride gas as low as 4 to 6 mg. per cu. ft. for 30 minutes to be lethal to several fungi and their spores. 1,2,3,4-Tetrahydronaphthalene showed promise as a fumigant against the webbing clothes moth, according to Colman.<sup>53</sup> Methods claimed to be more accurate than those now in use for the determination of naphthalene in insecticides are described by Miller.<sup>223</sup>

**Attractants and Repellents.** Metzger, van der Meulen, and Mell<sup>219</sup> found that plant extracts with a fruity odor were much more seriously infested with the Japanese beetle than those without such an odor. Metzger<sup>218</sup> found that phenylethyl alcohol increased appreciably the attraction of the geraniol-eugenol bait used in traps to capture the Japanese beetle. Eyer<sup>85</sup> reported that isobutylphenyl acetate and commercial rum ether, which are among the esters formed in fermenting sugar and vinegar baits, were the most consistent in their attraction of the codling moth in southern New Mexico. Frost<sup>98</sup> tested 40 chemicals for their efficiency in attracting the oriental fruit moth. Linalool, safrol, propyl acetate, amyl acetate, anethol, fennel seed oil, terpinyl acetate, and furfural were promising. Safrol is the most satisfactory

material to be added to five percent syrup solution to attract the moths. Hoskins and Craig<sup>159</sup> studied the olfactory response of blowflies (*Lucilia sericata*) to various concentrations of secondary amyl mercaptan and of methallyl thiocyanate. Price<sup>255</sup> repelled codling moths from fruit trees by spraying with a mixture of naphthalene and oil emulsion. Dove and Parman<sup>77</sup> recommended treatment with benzene to kill screw worm larvae in wounds, and pine tar oil as a repellent to the flies. Herrick<sup>153</sup> reported that *p*-dichlorobenzene, naphthalene, and cedar oils are repellent to clothes moths, but according to Abbott and Billings<sup>5</sup> these are useless for that purpose. de Ong<sup>241</sup> found that a coating of calcium carbonate protects stored rice against weevil injury. Flint, Farrar, and McCauley<sup>93</sup> reported that chinch bugs are strongly repelled by the odors from crude naphthalene or creosote, and Flint, Dungan, and Bigger<sup>92</sup> presented recommended specifications for creosote for chinch bug barriers. Moore<sup>227</sup> discussed the effectiveness of a number of esters as repellents for the house fly. The best materials were a very slightly volatile unsaturated cyclic ester, such as the dialkyl phthalates, and the pyrethrins. A formula for a commercial fly spray has been developed.

**Nicotine.** Richardson, Glover, and Ellisor<sup>262</sup> found that pyridine, piperidine, and nicotine in vapor form can pass directly through cuticula of insects. Kitchel and Hoskins<sup>182</sup> determined the toxic dose of nicotine vapor to the cockroach to be 0.005 mg. per gram of body weight. The addition of a little carbon dioxide increases the toxic effect of nicotine. Smith<sup>303</sup> reported that it is possible to kill codling moths in trees with nicotine vapors produced by atomizing a solution of 95 percent nicotine in kerosene, gasoline, or petroleum ether, but the method is not economically practical. Smith and Persing<sup>304</sup> later reported that it is possible to kill codling moths in an orchard by the use of 15 to 30 cc. of 50 percent nicotine per tree, applied when the atmosphere is calm. Thomas<sup>318</sup> found that nicotine fumigants, dusts, or sprays gave satisfactory control of springtails attacking mushrooms. The effect of sodium and potassium chlorides and bicarbonates on the paralytic activity of nicotine solutions for cockroaches was studied by Levine and Richardson.<sup>192</sup> Steiner<sup>311</sup> reported that nearly all soaps with nicotine sulfate gave a high immediate kill of the white apple leafhopper, but the residual kill varied with the kind and amount of soap. A correlation existed between high residual kill and the amount of nicotine recovered from the foliage. O'Kane, Westgate, and Glover<sup>239</sup> determined that the action of nicotine on mosquito larvae is not proportional to its concentration alone, but is indirectly associated with absorption phenomena. Richardson<sup>263</sup> found the deposit left by a nicotine sulfate-molasses spray to be the most effective of eight nicotine-spray residues tested for the control of the gladiolus thrips. Eddy<sup>83</sup> made a study of pine tar and pine tar oil in water-soluble form in the hope of finding chemical activators or accelerators for nicotine. The Bureau of Entomology and Plant Quarantine<sup>3</sup> has issued directions for the preparation of

insecticidal spray solutions from tobacco. Smith<sup>297</sup> studied the base exchange reactions of bentonite with salts of nicotine and other organic bases. Nicotine forms a definite compound with bentonite. Swingle<sup>315</sup> tested six substances containing nicotine in relatively insoluble and non-volatile form and water-soluble nicotine bitartrate against lepidopterous larvae. Nicotine silicate proved the most toxic of the fixed-nicotine preparations, surprisingly so because of its extreme insolubility. Driggers<sup>79</sup> reported that bentonite-sulfur fixes and sticks the nicotine of nicotine tannate and nicotine sulfate to apple foliage more firmly than when the nicotine compounds are used alone, thus increasing the effectiveness as a control for the codling moth.

The following nicotine products were patented: nicotine 2,4-dinitro-6-methyl (or phenyl or cyclohexyl) phenolate, by Mills<sup>224</sup>; and nicotine alginate and nicotine abietate, by Lindstaedt.<sup>194, 195</sup> Mewborne<sup>220</sup> patented the preparation of an insecticidal product from tobacco, and Inman<sup>168</sup> a product resulting from the reaction of  $\alpha$ -nicotine with a sulfonated partially oxidized petroleum hydrocarbon.

**Anabasine.** Smith<sup>298</sup> isolated anabasine from the root and leaves of *Nicotiana glauca*, a plant growing in Arizona. Nelson<sup>236</sup> prepared a sample of anabasine of high purity and determined some of its physical constants. Ginsburg, Schmitt and Granett<sup>113</sup> found that anabasine sulfate equals or exceeds nicotine sulfate in toxicity to a number of aphids, whereas it is much less toxic than nicotine sulfate as a stomach poison for silk moth larvae and grasshoppers. Garman<sup>102</sup> reported that sprays of anabasine sulfate gave satisfactory kills of the white apple leafhopper.

**Pyrethrum.** In California pyrethrum insecticide manufacturers are requested to give on their labels the percentage of pyrethrins and of inert ingredients.<sup>1</sup> Seil<sup>287</sup> described a method for the estimation of pyrethrins. Gnadinger and Corl<sup>116</sup> reported that pyrethrum samples showed a higher pyrethrin content when assayed by the Seil acid method than by the Gnadinger-Corl copper-reduction method. Haller and Acree<sup>134</sup> described a new method for the determination of pyrethrin II, which is based on the fact that it is the pyrethrolone methyl ester of chrysanthemum dicarboxylic acid and therefore yields methyl iodide when boiled with hydriodic acid. The methyl iodide is determined by the volumetric method of Vieböck and Schwappach as modified by Clark. Tattersfield<sup>316</sup> discussed methods of estimating the active principles of pyrethrum and results of cultural investigations. Experiments by the United States Department of Agriculture indicate that the cotton stripper can be altered to harvest pyrethrum satisfactorily.<sup>2</sup> Bake<sup>14</sup> reported that lead and solder react very rapidly with extracts of pyrethrum, decomposing the pyrethrins. These metals should not be present in containers used for storage. Hoyer and Weed<sup>164</sup> found that pyrocatechin, a so-called stabilizer or antioxidant for pyrethrum, protects the active principles of pyrethrum dissolved in kerosene only to a negligible degree. The deterioration of the active

principle of properly stored pyrethrum extracts is negligible for at least nine months. Voorhees<sup>326</sup> patented a process for making oil-soluble pyrethrum extracts stable against light by adding an amino-anthraquinone compound. Roney and Thomas<sup>277</sup> reported that pyrethrum-sulfur mixtures controlled the belted cucumber beetle and the bean leafhopper slightly better than did sulfur alone, but the margin of difference does not justify the extra cost. The percentages of control obtained with various pyrethrum-sulfur mixtures do not correspond to their pyrethrin content. Nelson<sup>235</sup> developed a cattle spray comprising a medium viscosity, neutral petroleum oil, pyrethrum extract, and diethyl phthalate, the last-named as a fly repellent. Searls and Snyder<sup>288</sup> found that 2 percent of an oil extract of pyrethrum adjusted to 2.1 percent pyrethrins was an efficient control of body lice on rats when applied by atomization, and destroyed about 81 percent of the mites present.

Pyrethrum products have been patented as follows: A process for the purification of pyrethrum extract, by Sankowsky, Grant, and Grant;<sup>283</sup> a mixture of pyrethrum extract and dibutyl phthalate in mineral oil, by Adams;<sup>6</sup> a mixture of pyrethrum extract and a furoic acid ester in mineral oil, by Adams and McNulty;<sup>9</sup> and a mixture of pyrethrum extract, a thiocyanate, and methylprotocatechuic aldehyde, by White.<sup>334</sup>

**Rotenone-bearing Plants.** Haller and LaForge<sup>135</sup> obtained crystalline deguelin in the optically inactive form only from a deguelin concentrate from derris root, but after catalytic hydrogenation some crystals of active dihydrodeguelin were obtained. LaForge and Haller<sup>189</sup> prepared and studied four isomeric isorotenolones. Jones<sup>173</sup> described the preparation of lonchocarpic acid, a new compound, m.p. 199° C., from the root of a species of *Lonchocarpus*. Gross and Smith<sup>128</sup> developed a colorimetric method for the determination of rotenone in the absence of isorotenone, deguelin, or dihydrorotenone, which utilizes the red color produced when an acetone solution of rotenone is treated with alcoholic potash and then, after an interval, with nitric acid solution containing sodium nitrite.

Gersdorff studied the toxicity to goldfish of optically active and optically inactive dihydrodeguelin,<sup>106</sup> and of acetyldihydrorotenone, acetylrotenolone, acetyldihydrorotenolone, and dihydrorotenolone.<sup>103</sup> By a consideration of the type of concentration-survival time curve obtained, he was led to propose<sup>104</sup> the minimum *ct* product (i.e., concentration  $\times$  time) as a criterion for comparing toxicities, and using this criterion in a comparison<sup>105</sup> of rotenone and seven of its derivatives, he demonstrated a quantitative correlation between changes in structure and changes in toxicity. Tischler<sup>320</sup> made studies on the respiratory process of insects together with other physiological studies, which strongly indicate that derris acts primarily by deranging the respiratory function in such a way that oxygen utilization by the various tissue cells is greatly inhibited. Fleming and Baker<sup>90</sup> reported that rotenone is inferior to, and dihydrorotenone dust is about equal to, acid lead

arsenate in effectiveness against the Japanese beetle. Ginsburg<sup>108</sup> found that residues from derris root, completely extracted with acetone, possess practically no toxicity to aphids, but are both toxic and repellent to caterpillars. The residue from derris root, extracted first with acetone and then with water, does not seem to possess direct toxicity to caterpillars, but acts as a deterrent to feeding. Granett<sup>123</sup> reported that ethyl alcohol was the only solvent which removed practically all the insecticidal substances from derris root. All other marcs tested exerted a deterrent effect on silkworms. Water-soluble organic solvents tend to extract more total solids from the root and also more of the active ingredients than do water-insoluble ones.

White<sup>337</sup> reported that derris dusts, home-mixed or commercial, containing from 0.5 to 1.0 percent of rotenone, gave the most satisfactory results of any of the insecticides (derris, pyrethrum, Paris green, calcium arsenate, and natural and synthetic cryolite) tested for cabbage worm control. Several non-alkaline diluents, including finely ground tobacco dust, finely pulverized clay, talc, diatomaceous earth, infusorial earth, and sulfur, proved satisfactory. Good control was obtained with a spray consisting of a derris root powder, containing 0.02 to 0.05 percent rotenone, suspended in water. Under some conditions a non-alkaline spreader or sticker was necessary. Sprays made by diluting pyrethrum or pyrethrum-derris extracts gave fairly satisfactory results. Hockett and Hervey<sup>165</sup> reported that the zebra caterpillar and the cabbage aphid were not satisfactorily controlled with derris or cube dusts. Derris and cube sprays and dusts have shown promise against thrips on cauliflower and against the Mexican bean beetle, but neither was satisfactory against the corn ear worm. Walker and Anderson<sup>330</sup> found that derris dust containing 0.5 percent rotenone gave satisfactory control of the cabbage looper and the larvae of the diamond back moth, the striped cucumber beetle, and adult squash bugs. Results against harlequin bugs were erratic. The Mexican bean beetle was satisfactorily controlled by a derris dust containing 0.75 percent rotenone. Derris dust was not successful against the corn ear worm, the potato flea beetle late in the season, or aphids. Walker and Anderson<sup>329</sup> reported that, of eight carriers for derris root dusts, talc gave the best control, closely followed by gypsum and a clay. Roney and Thomas<sup>276</sup> reported that a dust containing 10 percent of derris, or 0.5 percent rotenone, and 90 percent of 300-mesh conditioned sulfur was more effective and economical than any other dust or combination used for controlling cabbage worms. Campbell, Sullivan, and Jones<sup>41</sup> found kerosene pyrethrum extracts to be more effective in paralyzing flies, and derris extracts more effective in killing them. They also reported<sup>40</sup> that rotenone is not the only toxic constituent of kerosene extracts of derris and cube root, but that it is an important one. Lacroix<sup>188</sup> found both pyrethrum and derris to be highly toxic to the tobacco flea beetle, but the toxicity of these substances is lost in a few days after application to the tobacco plants. Ginsburg and Granett<sup>110</sup> reported that the



toxicity of derris root to aphids does not always bear a directly proportional relationship to its rotenone content, especially in samples containing large amounts of rotenone. Derris and cube roots are practically equal in toxicity to aphids, provided they contain approximately the same amounts of rotenone and total extractives. The combination of derris with lead arsenate, lime, or sulfur compounds caused derris to lose toxicity. Ginsburg, Schmitt, and Granett<sup>112</sup> found that water-soluble organic solvents, such as acetone and alcohol, are able to extract practically all the water-soluble and water-insoluble ingredients of derris root toxic to sucking insects. Anderson<sup>11</sup> reported that derris products give good results against the tobacco flea beetle on a small scale but in field tests do not afford permanent protection. Howard, Brannon, and Mason<sup>162</sup> reported the results of tests with derris against the Mexican bean beetle. Very good control was obtained with sprays at dosages of 1.5, 2, and 2.5 pounds of derris of 4.4 percent rotenone content in 50 gallons of water. At these dosages there is little or no saving of derris as compared with dust mixtures, but the better control and increased residual effect obtained with the water suspension make its use as a spray preferable. Water suspensions of the ground derris root are superior to the extracts of either derris or pyrethrum or a combination of the two. Roark<sup>268, 270, 271</sup> reviewed patents and literature relating to derris and cube, and Whittaker<sup>339</sup> reviewed the development of rotenone as an insecticide.

Jones<sup>172</sup> patented a process for making a chemical compound of rotenone and carbon tetrachloride consisting substantially in extracting the roots of plants of the genus *Derris*, *Lonchocarpus*, or *Spatholobus* with warm carbon tetrachloride and crystallizing. The following mixtures were patented: derris root with a sulfonated petroleum product, by James;<sup>169</sup> rotenone with pyrethrins, by Fulton;<sup>100</sup> and rotenone with a highly halogenated hydrocarbon in petroleum oil, by Buc.<sup>35</sup> Bousquet and Tisdale<sup>26</sup> patented a contact insecticide comprising a water emulsion of  $\beta,\beta$ -dichlorodiethyl ether, and an insecticide of the group consisting of water-insoluble dithiocarbamates, water-insoluble thiuram sulfides, and the toxic ingredients of derris root. Haller and Schaffer<sup>136</sup> patented a process for preparing dihydrorotenone by hydrogenating a rotenone-bearing plant extract dissolved in an organic solvent in the presence of a specially prepared nickel catalyst. Mills and Fayerweather<sup>226</sup> patented 1,2-dihydroxy-4-*tert*-butylbenzene and 1,2-dihydroxy-4-*tert*-amylbenzene for use as stabilizers for insecticides such as pyrethrum and rotenone.

Little<sup>196</sup> described ecological studies and experimental cultivation of *Cracca virginiana* in Texas. This plant can be made to yield as many pounds of roots per acre as derris. It can be grown on marginal land and produced for a few cents a pound. It is a nitrogen fixer, and its stems and leaves have some value as hay. Marked variations occur in the plants, indicating different varieties, or perhaps species. Physiological

tests are being conducted on these plants, to eliminate the poor and grow only the best, with encouraging results.

Jones, Campbell, and Sullivan<sup>174</sup> compared the toxicity to house flies of extracts of samples of derris root, cube root, haiari stem, and *Cracca virginiana* root with the values obtained on these samples by certain chemical determinations. The amounts of rotenone present in the samples were too low to account for all the toxicity. In more than half the samples the figures by the Gross-Smith test, considered as representing the sum of rotenone and deguelin, agreed with the toxicity value, but in the other samples they were lower. Total-extractive values were higher than toxicity, and values based on the methoxyl content of the extract, although somewhat closer, were also too high. When an approximate value for toxicarol was subtracted from the methoxyl figures, the results agreed more closely with the toxicity figures than did the results of other determinations. However, it is impossible, on the basis of the present results, to recommend unreservedly any one of these chemical determinations as a measure of the insecticidal effectiveness of rotenone-bearing plants. Further work is needed on this subject, particularly on the individual constituents present in such plant materials. Jones, Campbell, and Sullivan<sup>175</sup> made chemical and insecticidal tests on 32 samples of *Cracca*, mostly *C. virginiana*, collected in different parts of the United States. The relative effectiveness of kerosene and acetone extracts against house flies was tested. The two extracts were similar in effectiveness, and the acetone extract was well correlated with the degree of blue or blue-green color given by the Durham test. The insecticidal results were not well correlated with other chemical determinations. The most effective samples of *C. virginiana* root came from Texas. A sample of *C. latidens* root from Florida and one of *C. lindheimeri* root from Texas and seeds of the latter were highly effective. In spite of its lower content of toxic materials, it is believed that *Cracca* might be developed to an extent permitting competition with derris and cube. Roark<sup>269</sup> prepared a résumé of the information available up to April, 1934, on devil's shoe-string (*Cracca virginiana*).

**Croton Bean.** Spies<sup>306, 307</sup> found croton resin more toxic than rotenone to goldfish. Free hydroxyl groups rather than unsaturation are responsible for this toxicity and also for the vesicant action of the resin. Drake and Spies<sup>78</sup> studied the fatty acids obtained by saponification of croton resin, and Spies and Drake<sup>308</sup> isolated *d*-ribose from the croton bean.

**Tree Bands.** Davis<sup>68</sup> reported that bands treated with  $\alpha$ -naphthylamine were somewhat more effective than those treated with mixtures of tallow oil and  $\beta$ -naphthol in trapping codling moth larvae. Worthley<sup>346</sup> reported that corrugated strawboard bands treated with  $\beta$ -naphthol in lubricating oil appear preferable to untreated burlap bands for trapping codling moth larvae.

**Wood Preservatives.** Sweeney<sup>313</sup> patented a process for rendering moldproof a synthetic lumber prepared from cornstalks by treatment with copper sulfate solution before pressing and drying or by spraying with copper sulfate solution.<sup>314</sup> Conn<sup>54</sup> patented a process for protecting cellulose material comprising treatment of the degummed material with an aqueous solution of tannic acid and tartar emetic, dyeing with a bactericidal dye such as crystal violet, thioflavine-S, or malachite green, thereafter treating with an aqueous solution of potassium bichromate, copper sulfate, and acetic acid, and finally applying a cover treatment of tar. Another process of preserving fibrous cellulose materials, patented by Conn,<sup>55</sup> comprises treating the degummed material with a solution of tannic acid, then with tartar emetic, and finally with potassium bichromate. A protective reagent for cellulose material (Conn<sup>56</sup>) comprises tar and an oil-soluble residue resulting from the reaction of  $\alpha$ -naphthylamine with acetaldo. Bowen<sup>27, 28</sup> fastens creosote-saturated felt pads on top of wooden piles to preserve them. Derby and Cislak<sup>71</sup> introduce sulfur dioxide into wood and thereafter impregnate the wood with creosote oil to preserve it. Hartman and Whitmore<sup>142</sup> patented a composition to protect wood from fungi and insects comprising a water solution of a metal salt, a fluoride (e.g., sodium fluoride), an ammonium salt, and a material to hold metal salts in solution (e.g., hydrochloric acid). Andrews and Finlayson<sup>12</sup> protect fabrics from decay organisms by incorporating in the fabric a galvanic couple (e.g., Zn-Cu) which, when immersed in an electrolyte, produces soluble, poisonous compounds. Siever<sup>204</sup> impregnates cellulosic material with a mixture of creosote, acetone, and mercuric chloride. Other products patented as wood preservatives include a mixture of a petroleum hydrocarbon, an arsenic ester, and mercury naphthenate, by Merrill;<sup>216</sup> a mixture of creosote and an acid-treated, cracked pressure residuum, by Goodwin, Rearick, and Ferguson;<sup>121</sup> a mixture of turpentine and oil of tar for tree injection, by Yates;<sup>347</sup> and a mixture of kerosene, benzene, *o*-dichlorobenzene or naphtha containing about five percent  $\alpha$ -naphthylamine, by Calcott and Foreman.<sup>39</sup> Morrell<sup>230</sup> has patented a process for converting relatively high boiling coal-tar acids into lower boiling products which are suitable for use as wood preservatives and animal dip. Arsenical wood preservatives have been patented as follows: a mixture of diphenylamine and arsenic trichloride with an organic oil, by Walker;<sup>331</sup> and a mixture of a petroleum hydrocarbon, asphalt, arsenic ester, and mercury naphthenate, by Merrill.<sup>217</sup>

**Mothproofing.** The following mothproofing compositions were patented: petroleum naphtha containing 3-chloro-4-hydroxydiphenyl and a bonding agent of crude paraffin wax and stearic acid anilide to prevent crystallization, by Spokes;<sup>309</sup> a solution in an organic solvent of a compound of the formula  $C_6H_5-(x-C-x')_n-C_6H_5$ , in which  $x$  and  $x'$  represent hydrogen or alkyl groups, by Moore;<sup>229</sup> brucine

anilide in a dry solvent, by Ritter;<sup>286</sup> and a blue fabric impregnated with sodium arsenite, by Mucha.<sup>231</sup>

**Weed Killers.** Kiesselbach, Stewart, and Gross<sup>181</sup> reported that bindweeds are controlled in fields by treatment with sodium chlorate. The following products have been patented for use as herbicides: a solution of arsenious acid and concentrated sulfuric acid, by Rose;<sup>278</sup> a mixture of four parts calcium chlorate and one part calcium chloride, by Heath;<sup>146</sup> ammonium thiocyanate, by Sauchelli;<sup>284</sup> and a mixture of kerosene, heavy petroleum oil, and furfural, by Melhus.<sup>213</sup> The use of ammonium thiocyanate for soil sterilization for the eradication of potato wart disease was studied by Bell.<sup>20</sup>

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## Chapter XVIII.

### Gaseous Fuels. 1934 and 1935.

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Although, judged by the respective revenues reported for the two branches of the gas industry, the economic value of the manufactured gas distributed to customers still appears to exceed somewhat that of the natural gas so distributed, statistics<sup>1</sup> indicate that the total marketed production of natural gas, amounting in 1933 to over one and one-half trillion cubic feet, represented on the basis of volume over four-fifths, and on the basis of heating value, perhaps seven-eighths of the national production of gas of sufficiently high heating value for use as city gas. On the basis of energy, natural gas represented about 8.3 percent of the total national production of energy from all sources, exceeding that of anthracite and approaching, on the basis of the low thermal efficiency assumed, the fuel equivalent of the entire national supply of water power.

Of the enormous total recorded production of natural gas, by far the greater amount was consumed near the source, in large part for uses commanding but low unit prices, only about 347 billions, or about 22 percent, having been transported across state borders.

Based on reports of the Bureau of Mines,<sup>1</sup> the consumption of natural gas accounted for in 1933 was divided thus: domestic, 18 percent; commercial, 6 percent; industrial (including gas used in the field, in carbon black plants, electric public utility power plants, Portland cement plants and the like), 76 percent. The heating value of the gas listed under "field use" alone represents about three times that of the manufactured gas distributed to consumers by the gas industry. The total amount of gas wasted is unknown. It is stated that the waste of gas in the Texas Panhandle alone reached a billion cubic feet per day towards the end of 1933, representing a heating value more than twice that of the average total daily sales of manufactured gas to consumers by utilities.

In the same year, an amount of gas approximately equal to the recorded production of natural gas was treated for natural gasoline, yielding 1,420,000,000 gallons. Sales of propane, butane, pentane, and propane-butane mixtures reached nearly 39,000,000 gallons, a relatively small fraction, however, of the potential supply. Carbon black production amounted to over 269 million pounds.<sup>1</sup>

For 1933, of the total gas sales by utilities to consumers, 1,171,909,000,000 cubic feet, that distributed by natural gas companies comprised about 71.4 percent by volume and that distributed by manufactured gas companies, 28.6 percent, natural gas purchased and distributed by such companies representing about 3.5 percent of the total.<sup>2</sup> Thus, on a volume basis nearly three-fourths of the gas distributed to customers by utilities in the United States is natural gas; on an energy basis, natural gas constitutes over five-sixths of the total energy in the gas thus distributed. The revenues from manufactured gas continued, however, somewhat greater than those from natural gas distributed to customers, if returns from sales near the source for carbon black manufacture and the like are excluded.

Turning to the gas produced and purchased for distribution to consumers by the manufactured gas industry, we find for the same year <sup>2</sup> a total of approximately 367 billion cubic feet, of which water gas constituted 41.7 percent; coke oven gas produced by utilities 14.0 percent; coke oven gas purchased, 23.6 percent; retort coal gas, 8.0 percent; natural gas purchased, 9.2 percent; reformed oil refinery gas, 1.2 percent; oil gas, 1.0 percent; and reformed natural gas and butane-air gas each less than 1 percent.

There were used in 1933 in the manufacture of gas by utilities a total of 10,500,000 tons of solid fuels and 521,108,000 gallons of oil. Of the solid fuels used in the production of coke oven and coal gas in 1933, exclusive of that purchased from the coke and steel companies, 7,042,000 tons were carbonized and 786,000 tons were used for bench and producer fuel. Of the total of solid generator fuel of 1,743,000 tons, coke constituted 1,298,000 tons, or 74.5 percent; bituminous coal 399,000 tons, or 22.9 percent; and anthracite but 2.6 percent.

Statistical summaries from 1929 to, but not including, 1935 <sup>2</sup> show that both the natural and the manufactured gas industries have rounded the depth of the depression and are now on the rise. The lowest total sales of natural gas, exclusive of that used in field operations, manufacture of carbon black, by distributing companies in gas operations, or mixed with manufactured gas, occurred in 1932, amounting to about 808 billion cubic feet; the highest, 960 billion cubic feet in 1934, represents an increase of about 19 percent over this low. In the manufactured gas industry the total gas sold showed a low in 1933, amounting to 334 billion cubic feet. The high of 1930, 396 billion, was about 18 percent above this, and

the recovery in 1934, giving a total of about 347 billion, represents an increase of about 4 percent from the 1933 low. The revenues from both forms of gas passed through a low in 1933. For natural gas, the gain in revenue for 1934 over 1933 was about 6 percent; for manufactured gas the percentage gain in revenue was much smaller, amounting to only about 0.7 percent. Of the major manufactured gases, water gas production, which had been declining consistently prior to a low in 1933 when the production was about 153 billion cubic feet, rose 2.4 percent to nearly 157 billion in 1934. The output of coke oven gas made by utility companies was rising prior to 1932, when it declined, but not to the 1929 level. In 1933 and 1934 the production rose again, gaining nearly 5 percent in 1933 over 1932, and about 4 percent in 1934 over 1933. Retort coal gas output has been falling rather consistently since 1929, but showed a recovery of 1.6 percent from the 1933 low to a 1934 production of over 30 billion cubic feet. The production of oil gas, amounting to about one percent of the total gas manufactured in 1933, fell continuously, the decline from the year 1933 to the year 1934 being 12 percent, and was about the same amount for the year 1933 compared to 1932. Although the production of reformed natural gas, reported for the first time in 1933, contributed less than one-third of one percent of the total production of manufactured gas in that year, its jump in output of 110 percent in 1934 is of interest. Butane-air gas production, likewise amounting to a fraction of a percent of the total, continued to grow, that in 1934 amounting to about 28 percent over that of 1933.

The decreased production of manufactured gas has been in a considerable measure compensated for by the natural gas purchased, which has been steadily rising since 1929. In 1932 the amount of natural gas purchased increased to over 420 percent of that purchased in the preceding year. In 1933 the natural gas purchased was 24 percent over 1932 and in 1934 it was about 21 percent over 1933. The volume purchased during 1934 was over 41 billion cubic feet.

At the time of writing, the summaries for 1935 are not available, but trends for the total gas industry compiled through September<sup>a</sup> indicate that the revenues for 1935 will be higher than for 1934 but well below the 1929 level. The total sales of natural gas are, however, greater than for 1929, and the revenues from natural gas are comparable with those of 1929 for a similar period.

The foregoing statistics have a direct bearing upon the scientific developments relating to the industry, for with increased business the need of and support for such development increases. The rise in certain operations, as, for example, the reforming of natural gas, follows certain fundamental investigations and in turn promotes other studies of an allied nature.

## PRODUCTION AND OPERATION STUDIES

**Manufactured Gas.** *Water Gas; Reformed Gas.* The increasing use of natural gas is reflected in the technical studies of the industry, especially with respect to the manufacture of high B.t.u. gases with local equipment as substitutes for natural gas during peak load periods and emergencies such as line breaks. A thorough and timely survey of standby processes has been made by Willien,<sup>4</sup> who compares such processes with respect to the starting-up time, gas making capacity, force of operators required, and interchangeability of the resulting gas with the gas ordinarily distributed. Among the processes considered by Willien as substitutes for natural gas and manufactured gases are (a) the refractory screen oil gas process, (b) the Pacific Coast oil gas process, and (c) various modifications of the standard water gas process including, respectively, conventional operation with cracking of oil in the carburetter, cracking of oil in an atmosphere of steam, cracking of oil in the carburetter together with some cracking of oil through the generator fire either with or without the admixture of cracked butane, and finally by cracking butane in the carburetter, admixing the gas formed with blue gas.

The question of the rate of flame propagation of such substitute gases is, of course, an important one. Willien<sup>5</sup> cites the results of Ferguson, showing the presence of acetylene in high B.t.u. water gas made at high temperatures, amounting to as high as one-fourth of the illuminants, and the conclusion of the latter that the occurrence of the yellow tips in one appliance and flash back in another is due to the presence of acetylene and its high rate of flame propagation.

Willien,<sup>6</sup> in summarizing the status of standby gas processes, states that, for each kind of gas, some type of substitute gas has been developed or proposed and indicates that the Pacific Coast oil gas process appears to be adaptable in many cases. Johnson and Hemminger<sup>7</sup> have discussed the load conditions and the economics of the standby gas supply for systems distributing natural gas. Plant experiments on the utilization of a heavy oil, rather than gas oil, in the production of a high B.t.u. standby gas have been reported by Beard.<sup>8</sup> The operating practice of a standby plant of the refractory screen type has been described by Wehrle.<sup>9</sup>

Wiedenbeck<sup>10</sup> has reviewed the operating experiences in the production of reformed natural gas at the Chicago By-Product Coke Company, particularly with respect to handling of lampblack and gummy mixtures of tar and carbon. A report by Workman<sup>11</sup> on the use of high B.t.u. gas for standby purposes covers plant tests of the Laclede Gas Light Company, St. Louis, the Peoples Gas Light and Coke Company, Chicago, the Public Service Com-

pany of Colorado, and the Memphis Power and Light Company, together with a bibliography of oil gas processes by Willien.

Several reports on the reforming of natural gas are presented by the 1935 Gas Production Committee of the American Gas Association.<sup>12</sup> One plant reports that the formation of lampblack appeared wholly within the control of the operator and is a function of the relation of steam and natural gas through the generator. A mixture of blue gas and reformed natural gas of 400 B.t.u. per cubic foot and 0.38 specific gravity causes only a scum on the surface of the scrubber sumps and slightly fouls the purifiers. By increasing the steam slightly beyond what is usually termed normal, the lampblack can be eliminated completely at the expense of an increased density of the resultant gas. If the rate of flow of natural gas is increased, lampblack is produced in proportion and the density is lowered more than necessary, with a resultant increase in the cost. Studies of the determination of lampblack, fly ash, and tar in reformed natural gas have also been made by the committee.

Further plant studies of the reforming of natural gas in water gas sets have been presented by Young<sup>13</sup> with especial reference to the formation and removal of the lampblack formed. It was found that when lampblack was formed in the water gas set, deposits of a mixture of lampblack and very viscous tar not removable by steaming were formed in the relief holder and tubular condensers. Recirculation of hot water gas tar thinned with primary condensate from the light oil plant resulted in preventing stoppages in the tubular condensers. Experiments are described on the use of water and hot tar in the removal of lampblack from gas entering the relief holder. The substitution of a coke having a fusion point of 2300° F., for one having a fusion point of 2725° F., resulted in the almost complete elimination of lampblack and fly ash.

Experimental work directed toward the commercial recovery of carbon black produced in the reforming of natural gas in a water gas set without the use of steam is described by Willien.<sup>14</sup> Mulcahy,<sup>15</sup> in giving operating data on the production of reformed natural gas at Terre Haute, Indiana, describes the removal of lampblack by means of shavings boxes.

Perry<sup>16</sup> has patented the process of reforming refinery gases employing the combustion of a portion of the gas by means of pure oxygen introduced into the center of the gas stream to effect cracking of the remainder. Garner, Miller, and Leyden<sup>17</sup> treat natural gas by burning a portion of it, premixed with air up to the theoretical amount required for combustion, in a reaction zone maintained at about 800° C., through which the remainder of the gas is passed for the purpose of cracking it. The process is so carried out as to give a mixture of reformed gas and products of combustion of the desired heating value.

The use of refinery oil gas is discussed by Schaaf,<sup>18</sup> and by Work-

man,<sup>19</sup> operating results using other fuels than coke in a water gas plant by Jebb,<sup>20</sup> the use of steam during a blowrun by Willien,<sup>21</sup> and the use of a special oil of 19.5 A.P.I. gravity containing a large amount of wax by Eck.<sup>21a</sup>

Operating practice in the production of blue gas and its admixture with natural gas is discussed by Roberts.<sup>22</sup> Robison<sup>23</sup> describes the use of natural gas instead of, or simultaneously with, gas oil for carburetting blue water gas.

For economic reasons, the production of carburetted water gas from heavy oils still holds an important place among the industry's developments, as attested by a number of articles and patents. There has been a trend toward an increase in the proportion of oil used in the generator and the reforming of the oil through the fire to lower the specific gravity of the gas. The problem of handling heavy oil tar emulsions is apparently one besetting a large number of companies. Dashiell<sup>24</sup> has summarized the reasons for this situation, pointing out that most of the heavy fuel oils are residues from the distillation of asphaltic crude oils, that there is a tendency in most plants towards undercracking of at least some of the oil, that the tars produced are extremely viscous with resulting increased stability of the emulsions, and the reforming of the oil vapors through the fuel bed increases the viscosity of the tar because of the increased free carbon.

The character of the tar from water gas sets employing bituminous coal for the manufacture of uncarburetted blue gas in a water gas set has been improved by the introduction of water into the carburetter through oil sprays to maintain the temperature of the blue gas at about 1000° F. through the carburetter and superheater.<sup>25</sup> Parke<sup>26</sup> has described the alterations in plant and operation resulting from the changeover from the use of gas oil to heavy oil. The same writer has also compiled various experiences and expedients developed to cope with tar and emulsion problems.<sup>27</sup>

The continued interest in the use of heavy oils in water gas manufacture is indicated by the number of patents directed toward the use of such fuel in gas production. For example, in a process proposed by Terzian,<sup>28</sup> oil is vaporized, a portion of the product passing through an incandescent fuel bed to produce a reformed hydrocarbon gas, the other portion being cracked less completely, thus producing a mixed water gas and reformed oil gas. Another patent of Terzian<sup>29</sup> relates to the manufacture of a mixture of water gas and oil gas of low specific gravity, in which a portion of the water gas generated is burned and the heat stored to serve for vaporizing an increased quantity of oil, the oil vapors being reformed by passage through the fuel bed in the generator. Hall<sup>30</sup> proposes to increase the proportion of reformed oil gas in a mixed water gas and reformed oil gas. Attention to the problem of securing water gas tar of satisfactory character is shown in the patent

of Evans,<sup>31</sup> who proposes separate removal of the high free-carbon tar from the reformed gas made from heavy oil and of the tar of low free-carbon content from the unreformed carburetted water gas. Terzian<sup>32</sup> aims, in reforming natural gas or refinery oil gas, to insure the liberation of carbon taking place within the fuel bed, rather than in the gas space, thus producing a low gravity gas free from carbon black.

Interest in the use of heavy oil is further shown by the patents of Merritt and Koons<sup>33</sup> and of Nordmeyer and Stone,<sup>34</sup> on processes involving the use of oil in the generator and the use of a reverse air blast. Nordmeyer,<sup>35</sup> in a process employing the reversed air blast, specifies the passage of the major portion of the latter through the upper portion only of the fuel bed and its withdrawal circumferentially of the generator. Perry and Hall<sup>36</sup> have devised a process for the production of low gravity carburetted water gas employing a marginal blast. Perry<sup>37</sup> proposes a method of operating in which high-carbon oil is introduced on the top of the generator fuel bed and low-carbon oil in the carburetter during the uprun, the greater part of the high-carbon oil being introduced during the first half of the run and the greater part of the low-carbon oil during the latter part of the run.

Nagel<sup>38</sup> proposes a flash system of carburetting a lean hot gas. Morrell<sup>39</sup> has patented a process in which motor fuel is produced from coal and heavy oil in a flash distillation system involving partial condensation of vapors and of distillate products. A heavy oil is gasified as an emulsion in a patent of Ditto.<sup>40</sup> Blast furnace gas and the like are enriched, after heating, by means of atomized liquid fuel, followed by further heating before combustion with preheated air in a process of Mathesius.<sup>41</sup>

A process for the simultaneous production of a carburetted water gas and motor fuel is proposed by Sachs.<sup>42</sup>

Arnold<sup>43</sup> has suggested a process for coking heavy oils involving the addition of coke fines to the initial supply of heavy oil.

An experimental investigation by Elliott with Huff<sup>44</sup> has shown that sodium carbonate exerts a marked influence on the gasification of heavy oil in the presence of steam at temperatures encountered in water gas practice. Experiments were made on a laboratory scale with Bunker C oil cracked in the presence of steam at temperatures between 1300° and 1600° F., employing for comparison refractory surfaces of magnesite blocks both untreated and impregnated with 5 percent of sodium carbonate by weight. The use of sodium carbonate resulted in a decrease in the carbon deposited, a large acceleration in the steam-carbon reactions, a marked improvement in the thermal yield, and a decrease in the hydrogen sulfide formed per gallon of oil.

The production of high-hydrogen water gas from younger coal cokes has been the subject of an extensive experimental study by



Brewer and Reyerson,<sup>45</sup> dealing with the steam-carbon reactions, the effect of carbon dioxide upon cokes, and the effects of catalysts added to the fuel and of water gas conversion catalysts.

The removal of carbon monoxide from city gas is the subject of a patent by Perry and Fulweiler.<sup>46</sup> The passage of blue gas with steam through a reacting mass of ankerite, a native carbonate of calcium, magnesium, iron and manganese, for the elimination of carbon monoxide has been patented by Bössner and Marischka.<sup>47</sup>

Kunberger<sup>48</sup> has proposed the production of a low gravity water gas in a process involving the alternate reduction of iron oxide by blast gases and reoxidation of the iron by means of steam, with accompanying production of hydrogen.

That attention continues to be given to the possibility of employing pulverized fuel in the water gas process is indicated in the patents of Heller,<sup>49</sup> Duke,<sup>50</sup> and Air Reduction Company.<sup>51</sup> In the last-named patent, blue water gas is produced by supplying powdered coal or oil, together with oxygen, to a heated reaction chamber to which superheated steam, with or without a further fuel supply, is subsequently delivered.

Structural and operative features of water gas equipment are embodied in a number of patents.<sup>52</sup>

A number of departures from conventional forms of the water gas process appear in the patents of Hillhouse<sup>53</sup> on the continuous production of water gas, the continuous system of Lucke<sup>54</sup> involving the passage of metal balls through the fuel bed, and the continuous production of carburetted water gas,<sup>55</sup> employing producer gas, produced simultaneously, to supply the heat required for the process.

A new automatic control for water gas plants, as well as other cyclic operations, a portable blue gas set unit, a scroll tar separator, and further developments of the refractory screen process for gas of high heating value have been described.<sup>56</sup>

*Coal Gas, and Coke.* In a review of the progress in coal carbonization, gas-making, and by-product recovery in the 25 years previous to 1934, Porter<sup>57</sup> has pointed out that in 1934 the percentage of the total coal production carbonized was about the same as 30 years before—namely, 16.0 to 16.5 percent; that there has been no progress in the displacement of raw coal for steam generation by products of carbonization; and that the considerable increase in the use of coke and coal gas in domestic heating has been nearly counterbalanced by the decreased demand in the metallurgical industry arising from increased fuel efficiencies. The technical progress in the coking of coal has been marked, as evidenced by the increased output per unit cost due to the use of higher and longer ovens and of silica refractories, better design of flues, improved control of pressure inside the oven, underfiring with producer gas and blast furnace gas, steaming of the hot coke in the oven for a

short period, admixing fine coke or dust with the coal charge with consequent increased coke strength and lessened cost, and the development of dry quenching, and of vertical chamber ovens with gravity discharge.

Reference is made by Porter<sup>57</sup> to semi-commercial developments of the processes of Wisner and of Warner,<sup>58</sup> operating in the low temperature range.

Lavine,<sup>59</sup> in a comprehensive review of the properties characteristic of low-rank coals (lignite and sub-bituminous), outlines work on the destructive distillation and coking, as well as the dehydration, of such coals.

Recent developments in coal utilization for 1932-1933 are reviewed by Fieldner,<sup>60</sup> who refers to progress in this country and abroad in high temperature carbonization and the recovery of by-products, and the status of low temperature carbonization, hydrogenation and liquefaction of coal, hydrogenation of tar, and the synthesis of chemical products. Fieldner points out that the continued competition of cheap petroleum and natural gas has prevented application of new methods of coal processing, such as low temperature carbonization, because of the lack of adequate market for the liquid and gaseous by-products; that the technical process for hydrogenating and liquefying coal is now available and may be put to use when and if a failing petroleum supply requires the production of oil from coal, but that the process is too costly for use under present conditions; that a number of important chemical products, such as ammonia, methanol, higher alcohols, solvents, etc., are now being made from gases obtained from coal, but that even if all the ammonia and methanol consumed in the United States were made from coal, it would require only 0.15 percent of the 1930 production of bituminous coal.

Fieldner<sup>61</sup> reviews progress for 1933 in the preparation of coal, including coal washing, crushing, froth flotation of fine coal sludges, and briquetting, combustion of solid fuels, the use of automatic house heating furnaces adapted for use with summer air conditioning, the use of colloidal fuel, coal dust engines, high temperature and low temperature carbonization, and by-product recovery.

Three low temperature carbonization plants are cited as having been in operation during 1933 and 1934. Of considerable interest is the use of a modification of the Wisner process in a plant at Champion, Pennsylvania, having a capacity of 95 tons a day. In this process partial oxidation is employed to destroy the excess plasticity of high volatile, strongly coking coals. Oxidation of the coal is effected on rectangular multiple hearths. The carbonization is then completed in a rotor six feet in inside diameter by eighty-four feet long, the product being so-called coal balls. No by-products other than tar and gas are produced. A plant of the Lurgi

type is reported in operation in North Dakota and one of the Hayes type has been operated intermittently in West Virginia.

During the past year, the very comprehensive work on the gas, coke, and by-product making properties of American coals carried on at the United States Bureau of Mines in cooperation with the American Gas Association during the past few years has been summarized by Fieldner and Davis.<sup>62</sup> These tests, carried out on samples of coal ranging from 75 to 180 pounds in a metal retort, cover carbonization of 30 coals at 500, 600, 700, 800, 900, 1000, and 1100° C. and the yields and properties of the various products. These tests also include the study of one coal, both washed and unwashed. Unusually complete data are given, including, in addition to the usual proximate and ultimate analyses, ash fusion and calorimeter tests, analyses for sulfur forms, carbon dioxide, and fusain. Solvent extractions, rational analyses, and petrographic examinations, as well as determinations of the softening and plastic properties, agglutinating index, friability, and slacking properties were carried out. In addition, three standard assay tests—the Fischer, Fuel Research Board (Great Britain), and U. S. Steel Corporation—were employed. Commercial plant yields, available for eleven of the coals tested, showed good agreement of plant and test data.

Fieldner and Davis<sup>63</sup> have applied standardized laboratory methods for the determination of reactivity, electrical resistivity, hygroscopicity, ignition temperature and minimum air blast to representative cokes, made in large laboratory scale apparatus at carbonizing temperatures of 500 to 1100° C., from coals covering the entire range of coking rank. They present data to show that the coke becomes less reactive, less easily ignited, requires more air to sustain combustion, becomes less hygroscopic, and conducts electricity more readily as the carbonizing temperature is raised; that the reactivity as determined by the ignition temperature and minimum air required to sustain combustion is virtually a straight line function of the carbonizing temperature over the whole range; that cokes made at 500 and 600° C. conduct electricity hardly at all, but that between 600 and 700° C. there is a rapid increase in conductivity, with a tendency at carbonizing temperatures of 1000 and 1100° C. to approach a constant high value comparable with that of graphite.

Reynolds<sup>64</sup> points out that cokes made at low temperatures are considerably more hygroscopic than those made at ordinary by-product coke oven temperatures, being usually greatest for cokes made at 600 to 700° C.

The effects of the rate of heating and of the maximum temperature in the pyrolysis of a coking coal upon the yields and characteristics of the principal products are reported by Warren.<sup>65</sup> The yields of tar increase with increase in the rate of heating at the expense of the yield of gas and coke, the increase being proportional to

the ratio of the rates of heating. The conclusion is drawn that the mechanism of coking involves competition between distillation and decomposition processes, and that differences in the values of their temperature coefficients are responsible for the increase in tar yield as the rate of heating is increased. Davis and Auvil<sup>66</sup> have studied the effect of varying the free space over the charge upon the yields of gases and tars in the high temperature carbonization of coal in a series of experiments in the Bureau of Mines-American Gas Association type of retort, with free spaces corresponding to 3.9, 11.6, and 23.1 percent of the retort volume of 3.82 cubic feet. With increased free space, the yield of light oil at 900° C. increased 27 percent for an increased time of exposure of from 1.3 to 9 seconds, the benzene yield practically doubling and the paraffins disappearing. The gas yield was also increased. The neutral oils, aromatic liquids and tar acids in the tar decreased and the pitch and aromatic solids increased.

The effect of tempering coals of various ranks to moisture contents up to 14 percent, in carbonization at 800° C., was studied by Sherman, Blanchard, and Demorest.<sup>67</sup>

A comprehensive critical review of the chemical structure of coal has been made by Lowry,<sup>68</sup> who considers the molecular structure of coal as resulting from condensation and polymerization of polynuclear six-membered carbon ring compounds, and that this structure becomes more and more condensed in succeeding ranks of coal—peat, lignite, bituminous coal, and anthracite. The condensation of aromatic nuclei appears to be the main reaction in the solid residue during pyrolysis of coal and does not end until graphite is formed. Lowry regards solvent extraction, vacuum distillation, and low-temperature carbonization as representing increasing severity of thermal treatment of coal and yielding progressively simpler products. A comparison of a single coal by all of these methods is stated as an objective of the Coal Research Laboratory of the Carnegie Institute of Technology which should shed light on the mechanism of the thermal decomposition of coal.

A study of the primary decomposition and distillation of a coal *in vacuo* of the order of 10<sup>-3</sup> mm., using as a new research tool in this field a so-called molecular still in which the purpose is to ensure that the molecules from the coal surface neither collide with other molecules nor encounter a hot surface before being condensed on a cooler surface, has been carried out at the Coal Research Laboratory of the Carnegie Institute of Technology by Juettner and Howard.<sup>69</sup> Using this means for avoiding secondary decomposition of initial products, these workers have made a comparison of the condensates and gaseous products from high vacuum distillation of 20-40 mesh coal and of coal ground to a particle size of about 0.001 mm., with those from distillations at the same

temperature in a Fischer retort. The yields of phenols and of neutral ether-insoluble substances was studied. The conclusion is reached that, in the coal used, the simpler phenolic substances are produced from the neutral ether-insoluble substances.

The Pittsburgh Experiment Station of the Bureau of Mines has continued its studies of the gas-, coke-, and by-product-making properties of American coals.<sup>70</sup> Splint-coal bands from the Elkhorn bed in western Kentucky gave a higher yield and a stronger coke than was obtained from bright coal bands in the same seam. The yield and quality of gas from the two types of coal were nearly the same.

The expansion of coking coals is discussed by Altieri<sup>71</sup> who described a new type of coal expansion tester designed to permit simulating conditions affecting the expansion of the coal during carbonization in coke ovens.

Seyler<sup>72</sup> has reported that the addition of 8 percent of 20-100 mesh inerts to high volatile unwashed Klondyke coal prior to carbonization improved the physical properties of the coke, the best results being obtained with 6 percent of coke dust.

Meredith<sup>73</sup> has made a comparative study of materials used or proposed for the dustproofing of domestic coke.

A study of the gases liberated from Virginia coals at various temperatures is described by Fish and Porter.<sup>73a</sup>

Further data on the correlation of small and large scale carbonization tests are given by Selvig and Ode.<sup>74</sup>

The hydrogenation of coal is treated by Wright and Gauger,<sup>75</sup> together with the effect of partial hydrogenation on coking properties, and other topics in this field.

A number of patents on coal carbonization processes and equipment, assigned chiefly to the larger builders of coke ovens, have appeared. Among these are those of Still,<sup>76</sup> characterized by the withdrawal of the products of distillation from the interior of the coal charge, thus minimizing the secondary cracking reactions to give increased yields of benzol, an improved quality of tar, and reduced formation of naphthalene. Other patents have been granted on coke ovens<sup>77</sup> and accessories,<sup>78</sup> and special types of destructive distillation apparatus.<sup>79</sup>

The heating of regenerative coke-oven batteries by means of atomized tar oils or petroleum oils, using preheated air, is specified by Richardson.<sup>80</sup>

Various modifications of conventional types of carbonization processes have been proposed or carried out. Keillor<sup>81</sup> describes the operation of a plant at Vancouver in which coal gas is made in a given retort for the first twelve hours, water gas for the next four hours, and carburetted water gas for the last four hours. Miller<sup>82</sup> proposes a combined high- and low-temperature carbonization process producing a blended tar product, wherein the gases from

the high temperature coking of coal are brought in direct contact with coal to effect low temperature carbonization. Rose and Hill<sup>83</sup> have patented the use of a mixture of coal with naphthalene which is heated in a retort to the carbonizing temperature of the coal but below the critical temperature of the naphthalene, naphthalene and tar being separated from the coke after the carbonization. Bunce<sup>84</sup> describes the coking by means of hot gases of agglomerates of coke breeze and bituminous coal. Rose and Hill<sup>85</sup> have patented the treatment of coal and tar together in thin layers in the presence of steam, in which substantially all the tar oils are vaporized leaving a homogeneous mass of undecomposed coal and pitch suitable for gas manufacture. The passage of oil refinery gas through coal undergoing carbonization with resultant cracking is patented by Odell.<sup>86</sup> The coking of pitch and coal in a by-product coke oven battery is provided for by Tiddy<sup>87</sup> through the use of heat resistant metal linings in those ovens used for coking pitch. Other patents cover the production of coke and gas from oil in a retort,<sup>88</sup> the gasification of powdered fuel in an externally heated oven with production of rich gas and water gas,<sup>89</sup> and the continuous production of coal gas in a vertical retort with zones of gradually increasing temperature.<sup>90</sup>

Wisner<sup>91</sup> specifies the partial oxidation of finely divided coal by preheating it to about 175 to 235° C. to prepare it for coking. Another patent by Wisner<sup>92</sup> relates to the rotating heating drum equipment and associated cooler for production of carbonized coal balls.

The production of low-boiling liquid hydrocarbons by heating bituminous coal, peat, or lignite with an alkaline acetate has been patented by Michot-Dupont.<sup>93</sup>

Kemmer<sup>94</sup> describes apparatus for the utilization of the waste heat of coke-oven plants or gas works for refrigeration for gas purification. Suggestions for the improvement of the operation and maintenance of coal gas retort benches are given by Niles.<sup>95</sup>

**Gas Producers.** Weiss and White<sup>96</sup> have extended the work of White and Fox on the influence of sodium carbonate on the producer gas reaction and its possible use in the manufacture of water gas. This work involved studies of the reaction of graphite, treated with sodium carbonate, with air and with steam, employing slower cooling than in the earlier case in order to permit reversal of the reaction  $\text{Na}_2\text{CO}_3 + 2\text{C} = 2\text{Na} + 3\text{CO}$ , to which the observed effects are attributed. This reversal was almost quantitative in the region where the furnace cooled from 900 to 750° C. Although as little as 0.1 percent of sodium carbonate was effective in greatly increasing carbon monoxide production at 900° C., one percent of soda was ineffective with foundry coke, apparently because of the reaction of the soda with the ash to form silicates. Admixture of 5

880° C. than could be obtained from the untreated coke at 1090° C. percent of soda with the coke was effective, giving a richer gas at

Attention is called by Nagel<sup>97</sup> to improvements in the liquefaction and distillation of air and the availability of large capacity units for the production of oxygen and cites German costs for oxygen of 80 percent and of 95 percent purity.

**By-Products.** Porter<sup>98</sup> has reviewed changes affecting coke oven by-product recovery, especially the decline in revenue from ammonia resulting from the competition of synthetic ammonia, the recovery of sulfur from gas by the Koppers Thylox process and the possible use of such sulfur in the production of sulfuric acid for the manufacture of ammonium sulfate, and recent developments in the uses of tar products, in phenol recovery, and in the distillation of the coke oven tar by the sensible heat of the coke oven gas.

**Tar.** Dashiell,<sup>99</sup> in reviewing developments in heavy oil tar and emulsion handling, states that the use of heavy oil brings about a tar dehydration problem more acute than gas oil and that a tar dehydrating plant is a necessary adjunct to every water gas plant, whether it uses heavy oil or gas oil of the types available in large quantities, that is, asphaltic base oils. Such dehydration may be carried out (1) by heating in high, open tanks to 195° F., as described by Parke,<sup>100</sup> with subsequent treatment in stills, (2) by treatment in stills equipped for decantation, (3) by heating in closed tanks at up to 75 pounds pressure, and (4) by the use of centrifugal force. Operating and maintenance costs are given.

Zane<sup>101</sup> has described commercial apparatus for continuous distillation. Parke<sup>102</sup> discusses pressure flash dehydration and dehydration by spraying or pumping through restricted orifices. Zane<sup>103</sup> also describes automatic tar dehydration by heating under pressure and flashing into a column.

Morgan and Stolzenbach<sup>104</sup> have investigated the mechanism of tar emulsions and state that the emulsifying agent is primarily a hydrocarbon substance which appears in the emulsion as a membrane surrounding the water droplets and preventing their coalescence, that the toughness of this membrane determines the stability of the emulsion, and that the effect of the membrane may be increased by the presence of free carbon.

Numerous patents have been issued in the field of tar technology, especially as to recovery from gases,<sup>105</sup> tar distillation,<sup>106</sup> tar acids<sup>107</sup> and pitch.<sup>108</sup>

Delorey<sup>109</sup> reports an increase from 60 percent to 127 percent of rating obtained by the use of coal tar for boiler firing in place of slack coal.

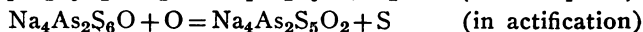
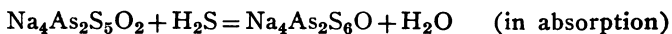
**Patents** issued in the by-product field cover carbon dioxide recovery,<sup>110</sup> acetylene removal,<sup>111</sup> benzene recovery,<sup>112</sup> ammonia recovery,<sup>113</sup> phenol recovery,<sup>114</sup> light oil absorption,<sup>115</sup> naphthalene

and anthracene,<sup>116</sup> and hydrogenation of carbonaceous materials.<sup>117, 118</sup>

Overall transfer coefficients for the absorption of ammonia and sulfur dioxide into a water spray, and the absorption of benzene vapor from air into an oil spray have been determined by Hixson and Scott.<sup>119</sup> This work also develops equations correlating the effects of variable fluid flows for use in spray tower design.

**Purification of Gas.** The developments in gas purification have related principally to improvements in liquid purification, the control of oxide box purification to minimize the escape of nitric oxide, and improvements in plant practice in the operation of oxide boxes.

The chemistry of the Thylox gas purification process has been studied by Gollmar.<sup>120</sup> Sodium or ammonium thioarsenate is the active agent in this process. The solution is regenerated by blowing with air. The principal reactions are believed to be



Unless the pH value of the solution is maintained at 6.7 or higher, the arsenic tends to revert to its lower valence and probably a mixture of arsenous sulfide and sulfur is precipitated. Sodium thiosulfate slowly forms from a little of the sulfur in suspension. The hydrogen cyanide in the gas is converted to sodium sulfocyanate. Carbon dioxide has practically no effect because of the low alkalinity of the solution. The toxicity of the solution, usually containing less than one percent equivalent  $\text{As}_2\text{O}_3$ , was studied but no evidence was found of arsenic poisoning.

Continued attention to the use of ammonia in liquid gas purification is indicated in the patents of Hansen,<sup>121</sup> of Davies,<sup>122</sup> and of Eymann.<sup>123</sup> The use of arsenic,<sup>124</sup> of non-aqueous solvents in conjunction with alkaline solutions,<sup>125</sup> of phenolates and the like,<sup>126</sup> of diethylenetriamine,<sup>127</sup> and other liquid purification processes are described in various patents.<sup>128</sup> The removal of carbon disulfide by a liquid process is the subject of a patent by Hansen and Eymann.<sup>129</sup>

The purification of natural gas containing small amounts of hydrogen sulfide in an iron oxide plant is described by Allyn.<sup>130</sup>

Brewer<sup>131</sup> has modified the method of Seil, Heiligman, and Clark for testing the activity of purifying material, by passing a part of the foul gas stream around the absorption solution, thus permitting the passage of a test gas containing 400 grains of hydrogen sulfide per 100 cubic feet to the glass absorption tower. With the gas quality and rate of flow constant, the amount of gas purified is a direct function of activity. This modified method showed that certain samples having the same capacity varied greatly in activity.

The use of granulated blast furnace slag for dry box purification is discussed by Presbrey.<sup>132</sup> Purifying materials for use in oxide



boxes have been patented by Seil<sup>133</sup> and by Smyly.<sup>134</sup> Broche<sup>135</sup> specifies the operation of oxide boxes in a two stage process involving the use of a somewhat elevated temperature and the controlled admission of oxygen containing gases in the second stage. Murphy<sup>136</sup> has reported that the addition of four to six grains of ammonia per 100 cubic feet of coke oven gas maintains the pH value of the drain water from the boxes between 7 and 8 and results in a greater activity of the oxide, complete removal of the hydrogen cyanide, and increase in the sulfur content of the spent oxide to as high as 56 percent.

Seil, Heiligman, and Crabill<sup>137</sup> find that the nitrogen oxide is held in relatively stable combination with fouled iron oxide sponge until after revivification and that the nitric oxide can be eliminated by blowing the sponge with air and steam at a relatively high temperature before re-use. Fulweiler<sup>138</sup> has described a patented method<sup>139</sup> of oxide box operation designed to prevent gum formation in gas distribution systems.

Seil, Heiligman, and Crabill<sup>140</sup> describe a procedure for conducting the Kunberger test on iron oxide for gas purification.

Other patents in the gas purification field refer to the use of sodium chloride solutions containing lime<sup>141</sup> and to the separation of sulfur from the sulfur dioxide of flue gases.<sup>142</sup> Further patents on the purification of gas at elevated temperatures have appeared.<sup>143</sup>

**Gas Storage.** The most radical development in gas holder construction appears to be that of a centrally guided waterless holder.<sup>144</sup> In connection with the operation of waterless gas holders, some attention has been devoted to possible substitutes for water gas tar as a sealant. For example, the use of a viscous solution of waste sulfite material from the digestion of wood by the sulfite process is proposed by Laue<sup>145</sup> and that of various specified viscous aqueous solutions by Sperr.<sup>146</sup> Gruse<sup>147</sup> proposes a heavy tar distillate from the tar produced in cracking a low-boiling petroleum distillate.

Unremitting attention has been given by the gas industry to the safety features of the operation and maintenance of gas holders. Theoretical and practical considerations in purging holders have been outlined by Tomkins.<sup>148</sup> Alrich<sup>149</sup> has discussed the maintenance of the M.A.N. holder with particular reference to the characteristics of the sealing fluid. Gas holder corrosion problems are summarized and discussed by Munyan,<sup>150</sup> who emphasizes the importance of periodical internal and external inspection as a safety measure. Inspection and maintenance of gas holders are covered in the Rules and Regulations of the New York State Department of Public Service.<sup>151</sup> Experience in the removal of sediment from the tank of a five-lift gas holder is described by Knowlton.<sup>152</sup>

Operation of a large gas holder in connection with a compressor station is described by Geiger.<sup>153</sup>

Dunn<sup>154</sup> has indicated the conditions making an underground reservoir suitable for natural gas storage, namely, that it has consistently produced gas according to Boyle's law, properly applied, and has not ceased producing.

**Purging.** The subject of purging gas plants, mains, and storage equipment has been given the closest attention by the gas industry. Specific instructions are given by the American Gas Association<sup>155</sup> for the purging of purifiers, and other gas works apparatus, including oil tanks, complete water gas plants, coal gas plants, gas mains, and works connections. Competent supervision, positive isolation of the container during the purging operation, an adequate supply of inert gas for purging, and reliable means for determining when the contents of the container are substantially free from gas or vapors are stressed. Definite directions for the production of inert gas are given.

Tomkins<sup>156</sup> has given a very complete discussion of the purging of apparatus with an inert gas, together with the explosive limits of different gases with air and maximum permissible oxygen and air contents of safe mixtures with inert gases. Carbon dioxide is indicated to be the most effective inert gas, and methods of producing it for this service are discussed.

**Natural Gas.** Comprehensive statistical studies of natural gas production have been presented by Swanson<sup>157</sup> and by Swanson and Struth.<sup>158</sup> Comparative natural gas production and consumption statistics for 1929-33 and for 1912, 1922, and 1930-32 are given by Hopkins and Backus.<sup>159, 160</sup> Further statistical data on natural gas are included in a review by Knapp.<sup>161</sup> Advances in the technology of natural and refinery gases, including the removal of hydrogen sulfide, gas transmission problems, natural gasoline plants, liquefied gas, carbon black, and gas cracking are outlined by Burrell<sup>162</sup> and Burrell and Turner.<sup>163</sup>

In presenting a review of technical developments in petroleum and natural gas production, Fowler<sup>164</sup> emphasizes the importance of the oil-gas-energy relationships, refers to conservation measures, including proration and unit operation, and reviews recent engineering research problems. These include methods of obtaining and interpreting subsurface pressures and temperatures in wells, solubility of gas in oil and the phenomena attending the liberation of natural gas under conditions approximating those of the reservoir, and the flow of oil, gas, and oil-gas mixtures through porous media, with particular reference to the problem of well spacing. Cattell and Fowler,<sup>165</sup> in a well-documented review, have discussed the recent work on fluid-energy relationships of petroleum and natural gas, and point out the value of such studies in the equitable allocation of production, the estimation of capacities of wells to produce

oil and gas, estimation of reserves, control of movement of gas, oil, and water within a structure, and similar problems.

Engineering factors in the conservation of natural gas are considered in a report of the Federal Oil Conservation Board.<sup>166</sup> Further discussions of the waste of natural gas<sup>167</sup> and of conservation measures<sup>168</sup> have appeared. Among recent studies referring to production are those relating to subsurface pressures and temperatures in flowing wells in the East Texas field,<sup>169</sup> solubility and liberation of natural gas from oil,<sup>170</sup> the energy liberated in isothermal expansion by gas-saturated oil sampled in high pressure bombs from within oil wells,<sup>171</sup> and the measurement of the permeability of porous media.<sup>172</sup>

Recent patents on chemical and other methods for treating gas and oil wells to maintain or increase production include those of Grebe and Stoesser,<sup>173</sup> Pitzer and Huffaker,<sup>174</sup> Boundy and Pierce,<sup>175</sup> Mills,<sup>176</sup> and Heath and Fry.<sup>177</sup>

A number of articles on the chemical treatment of wells,<sup>178, 179, 180</sup> drilling fluids,<sup>181, 182</sup> and the like have appeared.

Important contributions to the knowledge of phase equilibria in hydrocarbon systems have been made by Sage and Lacey<sup>183</sup> and co-workers, who discuss both simple and complex systems in the range of pressures up to 200 atmospheres and of temperatures from 20 to 100° C. Data are presented which permit the prediction of the density, composition, and relative mass of each phase present when a mixture of any total composition is brought to equilibrium at any set of temperature and pressure conditions within the range studied. Particular attention is paid to the methane-propane system<sup>184</sup> through the temperature and pressure ranges commonly found in underground petroleum formations, solubility of a dry natural gas<sup>185</sup> in crude oil, the solubility of propane in two different oils,<sup>186</sup> the pressure-volume-temperature relations and thermal properties of propane,<sup>187</sup> and the thermodynamic properties of pentane.<sup>188</sup>

The rates of solution of methane<sup>189</sup> and of propane<sup>190</sup> in quiescent liquid hydrocarbons have been studied experimentally by Hill and Lacey.

The economic aspects of gas-solubility experiments have been discussed by Morris.<sup>191</sup> Lacey<sup>192</sup> has likewise referred to the bearing of such studies on the practical problems of pressure maintenance in petroleum production.

Other papers dealing with the energy relations of natural gas and oil are those of Umpleby,<sup>193</sup> relating to the efficient utilization of reservoir energy, of Moore and Shilthuis<sup>194</sup> on the calculation of pressure drops in flowing wells, and of Hurst<sup>195</sup> on unsteady flow of fluids in oil reservoirs.

Conservation measures are reviewed by Lewis<sup>196</sup> and by Wallace,<sup>197</sup> who outlines practice in the protection of wells from

underground wastage and flooding. Eckert<sup>198</sup> describes practice in deep drilling in the Tioga and Potter County fields of Pennsylvania.

Neyman and Pilat<sup>199</sup> report that the heat of solution of natural gas associated with petroleum oils is of a very small order compared with the heat of compression, to which the thermal effects are practically confined.

The viscosity of natural gas has been determined for a number of natural gases of widely different chemical compositions by Berwald and Johnson,<sup>200</sup> through the use of the relationship between the friction factor and the Reynolds number for the flow of gas through pipes.

There has recently been reported the formation in natural gas transmission lines of solid compounds resembling snow or ice in appearance, which are attributed to the formation of hydrates with methane, ethane, propane, and isobutane in the presence of water at elevated pressures and temperatures. Hammerschmidt<sup>201</sup> has studied the conditions for formation of these compounds, as well as their melting points.

Considerable study has been devoted to the occurrence of gas in coal beds. Selden<sup>202</sup> has reviewed critically the factors involved, as well as theories as to the origin of the methane and carbon dioxide in such gas. Ranney<sup>203</sup> has patented a method for the recovery of mine gas and urges such recovery as commercially feasible. Lawall and Morris<sup>204</sup> have studied the occurrence of gas in Pocahontas No. 4 bed in southern West Virginia and have measured gas pressures and flows in holes bored into the coal. Burke and Parry<sup>205</sup> have developed mathematically the laws of flow governing the movement of gas in coal seams and discuss the origin of such gas.

The production and sales of natural gasoline and of liquefied petroleum gases are reviewed by Shea.<sup>206</sup> The huge potential supply of liquefied gases has led to a number of studies of means for their utilization. Oberfell<sup>207</sup> has reviewed progress in this direction with respect to their use as industrial fuels, in gas manufacture, and for domestic use. Gould<sup>208</sup> has made an economic study of this field. The use of propane and butane in the gas industry is reviewed by Friend.<sup>209</sup> The advantages of these fuels over fuel oil<sup>210</sup> for various purposes and of propane as a substitute for acetylene in the steel industry are presented by Jamison and Bateman.<sup>211</sup> Hunt<sup>212</sup> has described the use of propane in metal cutting and salvaging operations.

Experiences in substituting butane-air gas for 550 B.t.u. oil gas<sup>213</sup> and a description of a recent butane-air gas plant<sup>214</sup> have been given. A detailed description of typical butane-air gas plant equipment is given by Perrine.<sup>215</sup>

Patents on various processes and apparatus for generating gas

by carbureting air with liquid fuels have been issued.<sup>216</sup> De Florez<sup>217</sup> has patented a fuel for engines of lighter-than-air craft consisting of mixtures of hydrogen and butane and hydrogen and propane, respectively.

**Pyrolysis of Hydrocarbon Gases.** In addition to the reforming of natural gas and oil refinery gases in the production of low gravity gas for city use, considerable attention has been directed towards the chemical utilization of these gases.

In a review of the literature on the pyrolysis of saturated hydrocarbons with special attention to the primary decomposition reactions, Frey<sup>218</sup> points out that the paraffin hydrocarbons decompose chiefly into simpler olefins and paraffins and that high cracking temperatures favor the concomitant formation of complementary olefins and hydrogen. Two reaction mechanisms have been proposed. Surface catalysis dehydrogenates paraffins to the corresponding olefins or degrades them to carbon, methane, and hydrogen, converts cyclohexanes into the corresponding aromatics, and rearranges the other cycloparaffins. Storch<sup>219</sup> reviews critically data on the pyrolysis of methane, ethane, ethylene, gasoline, and petroleum to yield acetylene and has formulated mathematical expressions relating to the decomposition of methane. He has also discussed possible industrial processes utilizing the thermal decomposition of methane or ethylene diluted with 75 to 90 percent hydrogen or carbon dioxide. A survey is made of the recent developments in pyrolysis of unsaturated hydrocarbons by Hurd,<sup>220</sup> who proposes a mechanism correlating the fact that unsaturated hydrocarbons pyrolyze characteristically into (1) simpler products, (2) isomers which include branched chain hydrocarbons from straight chain members, (3) dehydrogenated members, and (4) polymers. The importance of the contact time and the influence of metal tubes are discussed.

The physical factors governing cracking operations are reviewed by Brown, Lewis, and Weber,<sup>221</sup> who outline methods, based on the pressure-volume-temperature relations of hydrocarbons, for computing the conditions existing at equilibrium, with special attention to the extrapolation of these methods, and their application to cracking plant problems. Paul and Marek<sup>222</sup> give velocity constants for propane, butane, and isobutane. Ipatieff, Corson, and Egloff<sup>223</sup> discuss a catalytic process for the polymerization of high olefin cracking still gases in the production of gasoline and mention a commercial plant which is in operation, producing more than five gallons of gasoline per 1000 cubic feet of cracking still gas.

The thermal decomposition of pentane is discussed by Morgan and Munday.<sup>224</sup> Lang and Morgan<sup>225</sup> have studied in great detail the pyrolysis of propane at low partial pressures. The results of their investigations show that a bimolecular primary decomposi-

tion occurs to a certain extent, that in the range of temperatures employed temperature has no effect upon the proportions of primary products obtained from propane, and that the proportion of propylene to ethylene in the unsaturated hydrocarbons obtained by commercial pyrolysis of propane may be increased at higher pressures. A critical study was made of the proposed mechanism of hydrocarbon pyrolysis, which is explained on the basis of Nef's dissociation hypothesis.

Among the patents in the field of pyrolysis of hydrocarbon gases are those of Sullivan and Ruthruff,<sup>226</sup> whereby saturated hydrocarbon gases are cracked, the methane and non-hydrocarbon gases eliminated by the selective absorption in oil of the hydrocarbons higher than methane, which are then polymerized at elevated temperatures and pressures to give a gasoline of high anti-knock properties. Another patent of Sullivan and Ruthruff<sup>227</sup> covers the polymerization of light olefins in a continuous system in the presence of naphtha, gas oil, or the like, at temperatures above 650° F. and pressures above 500 pounds per square inch to give gasoline of high knock rating. Wilson<sup>228</sup> has specified a process for the polymerization of unsaturated hydrocarbons at elevated temperatures and pressures. The production of liquid aromatic hydrocarbons from cracking still or coke oven gases by polymerization in a pipe coil, with immediate introduction of cooling oils into the heated gas to check conversion, followed by the rectification and condensation of the products is claimed by Egloff.<sup>229</sup> In another patent Egloff<sup>230</sup> proposes to crack natural gas or refinery gas, following the primary cracking operation with a secondary cracking at increased pressure and temperature in the presence of steam and hydrogen preactivated by an electric discharge. Plummer<sup>231</sup> proposes to combine the processes of polymerization of unsaturated hydrocarbon gases and the cracking of petroleum in a single process. Other processes are those of Wagner,<sup>232</sup> Egloff,<sup>233</sup> Dunstan and Wheeler<sup>234</sup> and Youker<sup>235</sup> for the polymerization of natural gas or oil-cracking gases.

A process for the production of light oils, wherein natural gas or oil still gases are so cracked as to give the optimum yield of aromatic hydrocarbons, and the resulting tars and residual gases then hydrogenated catalytically, is specified by Smith and Rall.<sup>236</sup> Odell<sup>237</sup> specifies a process in which gases containing unstable olefins are converted into stable hydrocarbons, employing firebrick with or without aluminum phosphate, aluminum oxide, iron oxide, or thorium oxide as catalysts.

The production of a gas rich in hydrogen by the catalytic conversion of hydrocarbons with steam is patented by Russell and Hanks.<sup>238</sup> A catalyst for this purpose is specified by Davis and Franceway.<sup>239</sup>

Among the patents for producing gas primarily for use in

internal combustion engines are those of Reichhelm,<sup>240</sup> Lacassagne,<sup>241</sup> and de Grey.<sup>242</sup> Apparatus for generating fuel gases from liquid fuels and air are patented by Jagmin<sup>243</sup> and by Cordes.<sup>244</sup>

Garner<sup>245</sup> has pointed out a number of possibilities and accomplishments in the chemical utilization of natural gas, including the use of an improved carbon black process which also yields hydrogen, the production of unsaturated hydrocarbons, the manufacture of formaldehyde from methane, the chlorination of hydrocarbon gases, the use of liquid butane as a solvent, and the recovery of bromine from brines from gas wells. Ellis<sup>245a</sup> has reviewed the chemical utilization of cracking gas, including a bibliography of 175 references.

Laboratory and plant data on the direct oxidation under high pressures of methane, ethane, propane, butanes, pentanes, and heptanes have been reported by Wiezevich and Frolich.<sup>246</sup> The products obtained may be separated into fractions having narrow boiling ranges. Oxidation of methane at relatively high temperature results in the production of some methanol. Higher hydrocarbons undergo a carbon-carbon scission during oxidation, with the formation of lower derivatives in high yields. By recirculating intermediate derivatives, acids are produced. Increase in pressure tends to lower the temperature at which oxidation takes place and to retard the decomposition of intermediate products. The authors include a bibliography of 93 references.

Recent patents on the partial oxidation of hydrocarbons under pressure for the production of alcohols and aldehydes include those of Walker.<sup>247</sup> Other patents refer to the production of acetylene,<sup>248</sup> of benzene,<sup>249</sup> and of hydrogen-nitrogen mixtures,<sup>250</sup> and to the removal of small amounts of oxygen from natural gas by a combustion method.<sup>251</sup>

The extensive investigations of Johnson and Berwald on the transmission of natural gas have recently been summarized.<sup>252</sup> Formulas for the flow of gas at high pressure in parallel lines have been included in this and other papers.<sup>253</sup> Problems in the design of natural gas transmission systems have been discussed by Merriam.<sup>254</sup> Van der Pyl,<sup>255</sup> in reviewing recent advances in the flow of fluids, has discussed the flow of natural gas at high Reynolds numbers.

A study of the values of discharge coefficients of square-edged orifices has been presented by Bean.<sup>256</sup>

**Problems in the Distribution of Gas.** Because of the large investment involved in the construction of distribution systems, the fixed charges on which constitute a great part of the cost of gas service, the problems of minimizing the investment costs and increasing the life of the system have received deserved attention. Of equal importance has been the problem of ensuring unfailing continuity of service. Many of these studies relate to problems of design and

construction which cannot be included here. Others, however, relating to the protection of the distribution system and to means for ensuring continuity of service involve problems of chemical interest.

The protection from corrosion of the enormous investment in underground pipe systems has been the subject of continued attention. Ewing<sup>257</sup> reports on a four months' field trip during the summer of 1935 to consult with gas engineers throughout the country and to remove and examine the third set of coated pipes which were buried in 1929 in the American Gas Association field coating tests, outlines the experience and practice of various companies with respect to pipe coatings, and offers suggestions for the logical attack on soil corrosion problems. Ewing<sup>258</sup> has also reported in some detail laboratory studies of the performance of pipe coatings in which periodic determinations of the electrical conductance of the coatings were made while they were exposed to the action of salt water and of soil which was alternately wet and dry. Among the important factors in estimating the protective value of pipe coatings are moisture penetration and the mechanical effect of the soil. These tests were designed to parallel field tests but with the end in view of developing a more rapid method.

Although much work is being carried out on protective pipe coatings, Turner<sup>259</sup> expresses skepticism as to the value of coatings in congested areas and points out the great care necessary to prevent bare spots in precoated pipe used in such locations. He states that, after a few years underground, the resistance of the coating may be reduced to zero and in many cases, particularly where stray current electrolysis prevails, the use of a coating invites rather than prevents corrosion, because of the restriction of the action to small areas where a break in the coating occurs.

The problem of electrolysis has received considerable attention. Ewing,<sup>260</sup> in a detailed report of the American Gas Association sub-committee on pipe coatings and corrosion, describes methods for making preliminary surveys and for determining where drainage stations should be located, where cathodic protection is employed, as well as for determining the effectiveness of the protection at any time after the installation is in operation. Bridge<sup>261</sup> has reviewed the cathodic protection of pipe lines and states that it has been demonstrated that a negative potential of 0.2 volt (net) pipe to soil will effectively prevent corrosion. Smith<sup>262</sup> has given an exposition in simple terms of cathodic protection of pipe lines and urges its more general adoption because of its simplicity and effectiveness. Schneider<sup>263</sup> has investigated the economics of such protection. Allyne<sup>264</sup> has reported on experimental work showing the practicability of intermittent electric drainage for pipe line protection. Kuhn<sup>265</sup> has likewise surveyed cathodic protection of pipe lines from soil corrosion.



Scott and Ewing<sup>266</sup> have studied the relative importance of the factors influencing the density of the pattern in the so-called pattern test for pipe coatings which depends upon the precipitation of ferrous (ferric) ion by ferricyanide or ferrocyanide ion on a suitable paper, which is then immersed in developing solution. The blue stains produced record the discontinuities in the pipe. An improved procedure adaptable to field conditions is specified. Ewing<sup>267</sup> has summarized work on pipe corrosion carried out during 1934. Abbott<sup>268</sup> has also discussed the present status of work of this type.

Although the emphasis has generally been placed on external corrosion, the problem of internal corrosion is receiving increasing attention, especially in connection with the transmission of natural gas. Allyn<sup>269</sup> points out that in California this type of corrosion is very serious, resulting from the action of hydrogen sulfide and oxygen in the presence of condensed moisture. Removal of hydrogen sulfide and oxygen by chemical methods is considered impracticable and dehumidification the only feasible solution. Schmidt and Bacon<sup>270</sup> have collected considerable information regarding the causes and effects of internal corrosion in natural gas transmission lines. The consensus of opinion appears to be that the most economical method of prevention now available is that of dehydration of the entering gas.

Brennan<sup>271</sup> has formulated a mathematical correlation of corrosion with the age and soil index for steel mains.

The corrosive effect of hydrogen sulfide on steel has been recognized as responsible for large economic losses, according to work of the Bureau of Mines.<sup>272</sup>

Although the increased use of mechanical joints for gas mains has tended to eliminate the hazards of broken mains, the bolts and nuts necessary for the joints are far more subject to corrosion and failure than the pipe itself. Perry<sup>273</sup> has recognized the importance of increasing the life of the bolts and nuts and has presented the results of an investigation directed toward this end.

During recent years, the use of automatically controlled gas appliances has increased rapidly, requiring the use of thermostats, safety pilots, and time controls. The corrosion-resisting properties of the metals employed in these appliances are of the greatest importance in their successful operation. Ward and Fulweiler<sup>274</sup> have made a study of the corrosion resistance of copper base alloys used in the manufacture of safety pilots and the like, when exposed to city gas containing organic sulfur at ordinary and slightly elevated temperatures (up to 275° F.), in the effort to find a corrosion-resisting alloy more readily machinable than aluminum. Alloys containing less than 63 percent copper and in sheet or rod form are almost perfectly resistant to corrosion resulting from the presence of organic sulfur and are further improved by the addition of one to two percent of either lead or aluminum. It was noted that

tubes of similar alloys, unless polished internally, were distinctly less resistant and the authors recommend that, pending the development of a commercially practicable method for cleaning the inside surface of tubing, aluminum tubing be used for installations where the tubing does not come in contact with alkaline insulation material, and that either tin plated tubing or a bimetallic tubing with aluminum on the inside and copper or brass on the outside be used where the tubing comes in contact with such material.

A discussion of the corrosion and oxidation of metals employed for gas appliance tubing, together with a bibliography, is given by Wright.<sup>275</sup>

The problems peculiar to high pressure storage and distribution in connection with gas supply to outlying districts have been studied by Larson.<sup>275a</sup>

The importance of ensuring continuous operation of automatic gas appliances and pilot lights has justified continued attention to the problem of eliminating the gums found to contribute, along with dust, to shortcomings in this respect.

In concluding the most recent of a series of papers describing an extensive investigation of the subject, Ward, Jordan, and Fulweiler<sup>276</sup> emphasize the importance of vapor-phase gum as a cause of pilot outages and malfunctioning of automatic gas appliances and attribute the formation of such gum to the action of oxides of nitrogen, largely nitrogen peroxide, on any of a number of organic compounds present in manufactured gas. The oxides of nitrogen, arising primarily in any type of manufactured gas from products of combustion, are present chiefly as nitric oxide, which is slowly oxidized to nitrogen peroxide, which then reacts rapidly to form gum. Vapor phase gum, existing dispersed in the gas in the form of a very large number of electrically charged particles of submicroscopic size, coalesce until a size of 1 to 1.5  $\mu$  is reached. Above this size they no longer remain so dispersed. The authors recommend the reduction of the concentration of nitrogen oxides to below 0.0003 grain per 100 cubic feet, equivalent to five parts per billion by volume, to ensure freedom from formation of vapor-phase gums and announce the development of a process involving a modified oxide box operation for ensuring the removal of nitrogen oxides by contact with sulfided iron oxide.<sup>277</sup> Further papers on this subject are those of Fulweiler<sup>278</sup> and that of McElroy with Brady<sup>279</sup> on the continuous addition of nitric oxide to city gas for use in accelerated tests of pilots.

Powell<sup>280</sup> has discussed the principles underlying the selective absorption of liquid phase gum-formers and naphthalene by oil scrubbing.

In a study of the effect of fogging oil on gum deposits, Mathias<sup>281</sup> reports laboratory and plant tests on the use of a fogging oil containing an inhibitor in order to prevent gum formation.

Patents have appeared relating to removal of gum-forming constituents from gas by solvents<sup>282</sup> and by an electric discharge,<sup>283</sup> the prevention of gum formation<sup>284</sup> by the addition of inhibitors to the gas or to meter oil, and the humidification of the gas in the mains to inhibit gum formation.<sup>285</sup> The use of an aftercooler and a Blaw-Knox gas cleaner to prevent deposits believed due to liquid phase gum-formers has been discussed by Tenney.<sup>286</sup>

Shnidman<sup>287</sup> has made a timely study of the problem of dust in gas, which appears to be more important at present in the transmission of natural gas than that of manufactured gas.

Experiments on the resistance to dust stoppage of various pilot orifices are reported by Corfield.<sup>288</sup>

Investigations of combustibles in manholes in Boston, Massachusetts, covering the findings of over 12,000 tests in Boston Edison manholes and over 3,000 manholes of the New England Telephone and Telegraph Company are reported by Jones.<sup>289</sup> Knowlton,<sup>290</sup> points out that notable progress has been made in eliminating explosion hazards and toxic conditions as a result of the cooperative effort of telephone, electric, and gas companies, and the U. S. Bureau of Mines. Statistics regarding carbon monoxide poisoning from various sources are cited by Briggs.<sup>291</sup> In a study of factors affecting the lethal action on experimental animals of mixtures of city gas with air, Smith, McMillan, and Mack found that the survival time was less in young adult rats than in old animals, and in male than in female rats, and that pregnancy and the use of a metabolic stimulant ( $\alpha$ -dinitrophenol) greatly reduced the lethal interval.<sup>292</sup> Barker<sup>293</sup> gives a case history of carbon monoxide poisoning from a smoking oil stove. Studies of the "normal" carbon monoxide content of the blood, supported by tests of the blood of dwellers of both city and rural districts have been made by Gettler and Mattice.<sup>294</sup> The average proportion of the hemoglobin combined with carbon monoxide was, for 18 persons in New York City under minimal conditions of exposure, 1.0 to 1.5 percent; for 12 institutional cases in a rural locality, less than 1.0 percent; for 12 street cleaners, about 3 percent; and for two taxi drivers from 8 to 19 percent.

A test is reported by Corfield<sup>295</sup> in which exposure to an atmosphere containing 24-29 percent of natural gas with the oxygen content reduced to 14-16 percent for a period of one hour and 15 minutes in a tightly closed room resulted in no injury to any of five men acting as subjects. Diffusion characteristics in gas leaks and the possibility of explosive mixture formation were also studied.

Klar<sup>296</sup> has reviewed the leather characteristics and defects of meter diaphragms, giving consideration to the value of various oils and diaphragm dressings. Some of the engineering aspects of diaphragm meters have been treated by MacLean.<sup>297</sup> Several articles

have been published concerning meter repair shop practice,<sup>298</sup> and factors and trends in meter maintenance.<sup>299</sup>

A patent has been granted to Fulweiler and Jordan<sup>300</sup> for a material for gas meter diaphragms, consisting of leather stuffed with soap composed of aluminum and saponified coconut oil, which is insoluble in benzene and other hydrocarbons normally present in gas drip and also insoluble in water.

The effect of humidity on meter proofs has been discussed by Corfield,<sup>301</sup> and in a report of the Pacific Coast Gas Association.<sup>302</sup> Bean describes<sup>303</sup> a convenient procedure for testing laboratory wet meters.

Zoll<sup>304</sup> has been granted a patent for an apparatus for determining the amount of "corrected gas" in a stream of raw gas such as producer or water gas.

Among the general reviews of developments in gas distribution are those of Battin<sup>305</sup> and of Larson.<sup>306</sup>

**Utilization.** The principal developments in the industrial utilization of gas have related to the design and construction of equipment for giving the proper gaseous atmospheres in which to carry out a wide variety of metallurgical operations. Equipment installed in industrial plants for the cracking, washing, and refrigeration of natural or manufactured gas has resulted in important new uses of gas where the effect of the atmosphere, whether oxidizing or reducing, is of importance. Considerable progress has been made in the use of controlled atmospheres in carburizing and other heat treating furnaces. A new development<sup>307</sup> is the use of so-called radiant tubes of alloy steel in which combustion takes place over a considerable length. Tubes of this kind have found considerable use in steel mills in the large annealing boxes for treating sheets and plates.

A continuation of the integration of the industrial uses of gas in the production lines of manufacturing processes has been observed. Typical examples of such applications, together with numerous references to the improvement of forging, hardening, and carburizing, to the bright annealing of copper tubing and of other non-ferrous metals, the melting of brass and soft metals, various low temperature baking and drying operations, melting of glass, vitreous enameling, the preparation of food products, industrial steam applications, and the like may be found by reference to the extensive annotated bibliographies appearing from time to time in the American Gas Association Monthly.<sup>308</sup>

Relatively little theoretical work appears to have been accomplished with respect to such subjects as the transmission of heat by radiation in furnaces, notwithstanding the fundamental importance of accurate knowledge of the temperature distribution in furnace design. Substantially all attempts to formulate equations covering the rate of heat transfer by radiation are based on the

wholly empirical Hudson-Orrok equation developed in connection with boiler furnace design. There seems little evidence that the highly mathematical treatments suggested by various investigators for the prediction of the distribution of radiant heat in furnaces have found any important engineering application, chiefly because of their complexity. There is little doubt that progress in furnace design has been greatly retarded by the lack of simplified design procedures. Hottel and Mangelsdorf<sup>309</sup> have presented data covering the absorption and emission of radiation from non-luminous gases and indicates very considerable changes in the magnitudes of these effects from those given in earlier publications.

Radiation from luminous and non-luminous natural gas flames has been studied experimentally by Sherman.<sup>310</sup>

Cowan<sup>311</sup> has discussed the development of heating, annealing, and other heat treating processes in controlled atmospheres with special reference to the use of diffusion combustion, in which the strata of air and gas travel parallel to each other throughout the furnace chamber without substantial turbulence, with the object of preventing oxidation by blanketing the metal undergoing treatment with a stream of raw gas. The use of methanol to prevent the formation of oxide films in the bright annealing of brass and the use of various hydrocarbon gases or hydrogen-liberating gases for the same purpose is mentioned. Segeler<sup>312</sup> has reviewed the recent work on special industrial furnace atmospheres, in which he refers to the necessity for consideration of the oxidizing effect of light amounts of oxygen and water vapor, methods for the detection of traces of oxygen, the desirability of oxidizing or reducing atmospheres in various processes, the factors influencing scaling or decarburization effects, the methods for obtaining the desired furnace atmospheres, and a list of specific recommendations regarding the type of atmosphere and methods for attaining the correct gas composition for various industrial heating operations.

Murphy and Jominy<sup>313</sup> have studied the influence of atmosphere and temperature on the behavior of steel with respect to scaling in forging furnaces and find that in a reducing atmosphere a higher temperature may be used. The scaling of steel increases with increasing time of exposure and temperature and is aggravated by the presence of small amounts of sulfur dioxide in the furnace gases.

Jominy<sup>314</sup> has studied the effect of pure gases including steam, carbon dioxide, air, nitrogen, hydrogen, and various synthetic mixtures of pure gases, the effect of pressure and that of rate of flow, temperature and period of exposure, of reducing and oxidizing atmospheres and the like on the surface decarburization of steel at heat treating temperatures.

Progress in the heat treatment of ferrous metals including

annealing, normalizing, bright annealing, carburization, and forging in connection with continuous furnaces in the automotive industry is reviewed by Clark.<sup>315</sup> Manier<sup>316</sup> has reported on the use of gas in the treatment of non-ferrous metals with special reference to the use of controlled atmospheres employing in certain cases gas preparation units for the cracking of gas to provide the desired conditions.

Gehrig<sup>317</sup> has discussed the application of gas-fired, radiant tubes to porcelain enameling. The results of experiments on 58 porcelain glazes employing direct gas firing in an oxidizing furnace atmosphere are reported by Watts.<sup>318</sup> It was found that both white and colored glazes can be direct-fired without damage either to body or glaze but that flashing or direct impingement of the flame against the glaze surface must be avoided. Direct firing results in a material reduction in firing time. Young<sup>319</sup> has described the bright annealing of non-ferrous metals and points out<sup>320</sup> the favorable opportunities for load building offered by the application of city gas for the production of special atmospheres in industrial furnaces.

Gillett<sup>321</sup> has made a valuable comprehensive review of controlled atmospheres in steel treating, covering the difficulties to be avoided by the use of controlled atmospheres, the effects of scaling, the properties of gases available for such use, reactions of gases with iron and carbon, various equilibrium data, cost and action of available gases, types of controlled atmosphere furnaces, correlation of experiments and experiences on scaling and its avoidance, decarburization, carburization, and bright annealing, the use of city gas for carburizing, and the like. A bibliography of 86 references is included. In a summary of this subject, Gillett<sup>322</sup> emphasizes the necessity of further research and points out unsolved problems in this field.

Among the various research projects pursued by the Committee on Industrial Gas Research<sup>323</sup> of the American Gas Association, are the studies of the effect of operating temperatures and of furnace pressures on the combustion of industrial gas, the development of individually heated and controlled deck bake ovens, the application of heat to ceramic firing, to sheet steel enamelling, ceramic decoration, and the development of gas operated house cooling and air conditioning equipment for both large comfort and industrial applications and smaller unit air conditioners.

Progress in the application of gas to summer air conditioning for comfort employing the silica gel method, as well as in the use of lithium chloride solutions for the dehydration of air, has been reported.<sup>324</sup> Among industrial uses of gas for air conditioning may be mentioned that in the printing industry, described by Fonda.<sup>325</sup> A detailed discussion of silica gel and its uses is given by Lednum.<sup>326</sup>

The possibilities of improving the character of the gas load by

the development of air conditioning by gas are discussed by Parker.<sup>327</sup>

King<sup>328</sup> has outlined the principal consideration in the conservation of heat in gas-heated buildings. A bibliography of 148 recent articles on house heating and cooling appears in a report of the House Heating and Cooling Committee of the American Gas Association.<sup>329</sup>

Methods of calculating gas heating have been presented by Kuenhold,<sup>330</sup> together with data on conditioned air heating. A graphical method for determining flue losses from industrial gas furnaces is outlined by Smith.<sup>331</sup> Data on the heat content of gases from 0 to 1900° C. have been given by Taylor.<sup>332</sup>

The importance of gas fuel in modern power generation has been pointed out by German<sup>333</sup> and by Philo.<sup>334</sup> A renewed interest in gas engines, after a long period in which their use was limited chiefly to blast-furnace gas plants and in oil and gas fields, has been noted. A tabulation, giving data on 33 new engine plants, the largest being of 6600 h. p. total capacity, is given by Tangerman.<sup>335</sup> The development of automatic gas engines for refrigeration and pumping purposes is receiving attention.<sup>336</sup>

A revival of interest in gas lighting, with especial reference to flood lighting and indoor industrial lighting, has taken place in the past few years and a number of notices of successful installations employing high pressure street lighting have appeared.<sup>337</sup>

Among papers relating to the design of domestic gas burners is that of Conner<sup>338</sup> and of Leonard and Howe,<sup>339</sup> who have established performance curves for a single port burner and a multi-port burner and suggest that it should be possible to interpret the form of such curves in terms of ignition velocity data. Mattocks<sup>340</sup> has discussed the factors affecting the design and application of industrial gas burners. Appliance testing and laboratory operation are described by Conner.<sup>341</sup> The function and design of draft hoods<sup>342</sup> and the operating characteristics of domestic gas pressure regulators<sup>343</sup> have been discussed by Smith and the venting of flues by Clow.<sup>344</sup>

Attention is given to the design and performance of safety pilots by Leighton,<sup>345</sup> to the resistance of range pilots to drafts by Smith,<sup>346</sup> and to the capacity of domestic flues and vents by Wills.<sup>347</sup>

**Combustion.** Morgan and Stolzenbach<sup>348</sup> have established experimentally that the ratio of the volume of carbon monoxide to that of hydrogen in products of combustion of carbonaceous fuels containing sufficient hydrogen is constant at 2.9 when the fuels are burned under such conditions that the free hydrogen in the incompletely burned products does not exceed 3 percent, thus confirming the conclusion of Minter,<sup>349</sup> who contended that, contrary to rather common opinion, hydrogen does not burn at high temperatures at a greater rate than carbon monoxide. Hamilton<sup>350</sup> has

described a device for exhaust gas analysis based on the constancy of the carbon monoxide:hydrogen ratio in automobile exhaust gases.

A study has been made of the combustion rate of carbon by Tu, Davis, and Hottel.<sup>351</sup> A quantitative formulation of the rate of combustion of carbon in air is given, based on the concept of a surface covered by a relatively stagnant film through which oxygen and combustion products must diffuse countercurrently.

The effect of ash on combustion characteristics of carbons has been studied by Oshima and Fukuda,<sup>352</sup> who present data on the effect of natural ash and of added salts in carbonaceous materials upon their ignitibility and combustion velocity.

The soap-bubble or constant pressure method as applied to the explosive oxidation of carbon monoxide has been described by Fiock and Roeder.<sup>353</sup> Results for this system of gases are reported over a wide range of mixture ratios. In an earlier report<sup>354</sup> the authors point out that water appears to be an essential factor in attaining equilibrium in this reaction.

The combustion of carburetted water gas in luminous flames has been studied by Altpeter and Kowalke.<sup>355</sup> The criterion of completeness of combustion was the carbon monoxide content of the flame. Combustion rates at which carbon monoxide was reduced to 0.2 percent varied from 208 cubic feet per hour for a ratio of furnace volume:furnace area ( $V/A$ ) = 16 to 132 cubic feet for ( $V/A$ ) = 4.

A review of various experimental determinations of the mechanism and rate of combustion of solid carbon by gaseous oxygen, a discussion of previous mathematical analyses of the process, and an account of some measurements at low pressures are given by Mayers,<sup>356</sup> who concludes that much more experimental work will be necessary before a complete formulation of the rates or mechanism of the reaction can be made.

In another paper, Mayers<sup>357</sup> discusses the mechanism of combustion in both pulverized coal and in grate firing, together with the characteristics of coals determining the attainable rating.

A marked catalysis of the oxidation of carbon, employing as catalysts lithium, sodium, potassium, strontium, and barium chlorides, and sodium and potassium sulfates, is reported by Day, Robey, and Dauben.<sup>358</sup>

Lewis and von Elbe<sup>359</sup> have calculated the theoretical explosion pressures for oxygen-hydrogen mixtures by means of thermodynamic functions of gases derived from band spectra and offer explanations for the difference between observed and calculated values in the cases of dried oxygen-hydrogen mixtures and in those containing excess oxygen or nitrogen.

Water vapor, in amounts above five mm. vapor pressure, has been found by Jones and Seaman<sup>360</sup> to raise the ignition tempera-



tures of methane-air mixtures slightly. The maximum increase, for a saturated mixture containing above 4 percent methane, was found to be  $11^{\circ}\text{C}$ .

A study by Pease<sup>361</sup> of the mechanism of the slow oxidation of propane at lower temperatures and oxygen concentrations than heretofore employed indicates that methanol, formaldehyde, carbon monoxide, and water are the primary products. Results are interpreted in terms of the radical-chain theory of Rice, on the assumption that methoxyl ( $\text{CH}_3\text{O}$ ) and propyl ( $\text{C}_3\text{H}_7$ ) are the chain carriers.

Benton and Bell<sup>362</sup> have made a study of the kinetics of the oxidation of carbon monoxide with a reduced silver catalyst in the range of  $80\text{--}140^{\circ}\text{C}$ ., together with the adsorptions of the three gases involved.

According to McKinney,<sup>363</sup> platinum oxide is a catalyst for the combustion of carbon monoxide at  $80^{\circ}\text{C}$ . and is not reduced as long as oxygen is in excess.

The activation energies of the reaction  $\text{O} + \text{H}_2 = \text{H}_2\text{O}$  have been studied by Bear and Eyring.<sup>364</sup>

**Composition and Analysis.** Among the papers relating to gas-works control and industrial problems are those of Willien,<sup>365</sup> of Glover<sup>365a</sup> and of Bermann,<sup>366</sup> the last including a number of nomographic charts. Jones and Kennedy<sup>367</sup> have investigated the values below which the oxygen must be maintained to prevent explosions of combustible gases and vapors and have given critical oxygen values for the paraffin hydrocarbons up to and including hexane and for ethylene, propylene, hydrogen, and carbon monoxide using carbon dioxide and nitrogen, respectively, as the inert diluents. The effect of elevation of temperatures for the range below  $40^{\circ}\text{C}$ . was studied.

Yeaw and Shnidman<sup>368</sup> have studied experimentally the dew point of flue products from the combustion of manufactured gas and find that the true dew points are higher than those calculated from the water estimated to be present according to the chemical equations involved in the combustion by an increasing amount as the excess air in the gases decreases, this result being attributable to the presence of a trace of sulfur trioxide in the flue products.

Scott,<sup>369</sup> in a review of methods of fuel calculations, has outlined the computation of the ultimate analysis of coal from B.t.u. content of fuel, percentage ash, and the composition of the flue gas. Other papers relating to the stoichiometry of fuels include those of Paul and Gleason<sup>370</sup> relating to engine exhaust gas analyses and their interpretation and application in the determination of air-fuel ratios and engine economy.

Anthes and Fahey<sup>371</sup> recommend the determination of such combustion data for gaseous fuels as the air requirements for combustion for a given gas or the volume of flue products by calcula-

tions based on the results of an explosion test of the gas in an Elliott apparatus and a determination of the heating value in a Junkers calorimeter with the measurement of condensate and analyses of calorimeter flue gas samples.

Charts have been presented by Nutting<sup>372</sup> for reduction to standard conditions of gas saturated with water vapor.

*Gas Analysis.* The developments in gas analysis have related chiefly to the use of physical methods, such as thermal conductivity through the increased use of micro-analytical methods, the development of automatic gas analysis apparatus, and the use of low-temperature methods. The use of the conventional absorption methods has been given attention by Kobe and Williams,<sup>373</sup> who discuss the merits of various confining liquids with respect to the solubility of carbon dioxide. They conclude that a solution containing 20 percent of sodium sulfate by weight and 5 percent by volume of sulfuric acid is the most satisfactory. Mulcahy<sup>374</sup> has discussed the application of exact gas analysis to gas plant problems, pointing out the variety of types of gas encountered because of the recent changes in the industry. Various possible sources of error and methods for their correction are given.

A new modification of the circular manifold type of gas analysis apparatus employing the Huff pumping pipette is described by Jones.<sup>375</sup>

Gas absorption apparatus has been described by Dillon.<sup>376</sup>

Further work on the micro-analysis of gases, using solid reagents, has been carried out by Blacet and MacDonald,<sup>377</sup> who have extended their earlier methods to include a new method for the determination of hydrogen and carbon monoxide, and to include hydrogen chloride and ammonia as gases determinable by the use of reagents already available.

The analysis of combustibles in flue gas has been discussed in detail by Evans and Davenport,<sup>378</sup> who have developed a gas analysis apparatus employing slow combustion and several novel details. An improved slow combustion pipette has been developed by Porter and Cryder.<sup>379</sup> Walker and Christensen<sup>380</sup> recommend the determination of methane by catalytic oxidation over cobalt oxide. A comparison of the Elliott and Hempel explosion apparatus, employing measured volumes of gas and air, has been made by Anthes and Fahey,<sup>381</sup> who conclude that the accuracy of the Elliott apparatus for use in routine gas plant practice may be made considerably higher than ordinarily assumed.

Branham and Shepherd<sup>382</sup> have made a critical study of the determination of ethane by explosion, employing pure oxygen, commercial oxygen, and air.

The sampling and analysis of entrained matter in gases, especially as a test of the efficiency of Cottrell precipitators, is discussed by Varga and Newton.<sup>383</sup> A new dew point apparatus for the deter-

mination of water vapor in natural gas which permits the test to be carried out in line under flow conditions, is described by Woodruff.<sup>384</sup> The determination of water and hydrogen sulfide in gas mixtures is discussed by Fraas and Partridge.<sup>385</sup>

Littlefield, Yant, and Berger<sup>386</sup> have described a hydrogen sulfide detector based on the color change reaction on the surface of granules coated with activated aluminum oxide with silver cyanide or lead acetate and placed in a glass tube through which the atmosphere to be examined is aspirated by a rubber bulb or hand pump.

Further use of the thermal conductivity principle for the analysis of gas is disclosed in the papers of Smith<sup>387</sup> and of Anderson<sup>388</sup> for the continuous determination of the helium content of natural gas.

Other apparatus employing electrical resistance effects are disclosed in the patents of Stein<sup>389</sup> and of Jacobson.<sup>390</sup> Schmidt<sup>391</sup> proposes to determine the oxygen content of flue gases and the like by carrying out combustion in the presence of an excess of flowing hydrogen and determining the temperature rise imparted to a separately metered stream of cooling fluid. Howe<sup>392</sup> proposes a method for determining oxygen in gas involving measurement of the temperature rise resulting from the catalytic reaction of the oxygen and combustible gas. An analysis apparatus for the determination of carbon dioxide in flue gas is patented by Brown and Harrison.<sup>393</sup>

A simplified design of carbon monoxide alarm and ventilation control is described by Houghten and Thiessen.<sup>394</sup>

An improved automatic analyzer for carbon monoxide in air in which the necessary removal of water vapor is accomplished by the use of silica gel or activated alumina is described by Frevert and Francis.<sup>395</sup> A simple carbon monoxide testing device has been described by Dunham.<sup>396</sup>

The increased interest in the utilization of cracking still gases and natural gas condensates has resulted in the direction of further attention to the low temperature analysis of hydrocarbon gases. Among the contributions in this field may be mentioned the method of Happel and Robertson<sup>397</sup> for the analysis of dry refinery gases below pentane by simple batch distillation employing a master graph whereby the composition of a refinery gas may be determined by an ordinary simple distillation of the condensed gas. Tropsch and Mattox<sup>398</sup> describe a low temperature fractional condensation method for determining the gasoline content of refinery gases. Lang<sup>399</sup> has employed a combination of the Podbielniak distillation column and the Shepherd apparatus in the analysis of complex gas mixtures encountered in the pyrolysis of propane. A method for determining ethylene, propene, and butene is outlined by Tropsch and Mattox<sup>400</sup> which depends on the fractional solution of propene and butene in 87 percent sulfuric acid, the density of the mixture of propene and butene serving to give the ratio of the two hydrocarbons.

The ethylene is determined by absorption in concentrated sulfuric acid activated with nickel and silver sulfates.

Podbielniak<sup>401, 402</sup> has described a fluid-reacting apparatus especially adapted for fractionation in which gravity has been replaced by centrifugal force, and in which a consequent remarkable increase in efficiency of fractionation is said to be obtained in the fractionation analysis of petroleum.

Fulweiler<sup>403</sup> has reviewed the analytical method for the determination of nitric oxide in city gas and summarized work carried out during the past five years. An apparatus has been developed for the automatic detection of nitric oxide in city gas.

*Various Analytical and Test Methods.* Kemp, Collins, and Kuhn<sup>404</sup> have shown that by refinements in the apparatus and its use, the effusion method for determining the specific gravity of gases may be greatly improved.

Considerable material of interest in connection with the analysis of gas making materials and by-products of gas manufacture is contained in the work of Fieldner and Davis,<sup>405</sup> Selvig and Ode,<sup>406</sup> of Kirner<sup>407</sup> on the microdetermination of carbon, hydrogen, and oxygen, of Merkus and White<sup>407a</sup> on the evaluation of gas oils, and of others.<sup>408</sup>

A method for determining moisture in coal is described by Wood.<sup>409</sup>

Berry<sup>410</sup> has analyzed the accuracy of humidity computations and points out that since very small errors in wet-and-dry bulb temperatures produce relatively large errors in determinations of humidity, there is no gain, in the absence of highly precise wet-and-dry bulb temperature measurements, in using the equations of Carrier or of Ferrel as compared with the much simpler equation of Apjohn, proposed about a century ago, and that, indeed, the use of the Apjohn equation, together with steam tables and the equation of state of air, may be more convenient for the occasional worker than that of established humidity charts. Ebaugh,<sup>411</sup> in agreement with the analysis of Berry, presents an air density chart, based on the Apjohn equation.

Among the papers presented before the Division of Gas and Fuel Chemistry at the 1935 New York and San Francisco meetings of the American Chemical Society are a number relating to analytical methods as yet appearing only in abstract form,<sup>412</sup> including those of W. A. Millikan, H. A. Cole and A. V. Ritchie on the determination of gaseous olefins or hydrogen by catalytic hydrogenation, of W. H. Fulweiler and C. W. Jordan on the development of practical methods for determining small quantities of nitric oxide in different types of gas, of E. S. Hertzog on the determination of arsenic in coal, of W. T. Reid on the effect of iron on ash fusion temperatures, of W. R. Kirner on the direct simultaneous microdetermination of carbon, hydrogen, and oxygen in coal and its

products, of C. C. Furnas on a new method for the determination of the reactivity of solid carbon, and of D. T. Bonney with W. J. Huff on the determination of hydrogen by liquid reagents, in which a new and active reagent consisting of colloidal palladium and of an organic acceptor which readily undergoes reduction and reoxidation is announced.

An investigation of the accuracy of the Junkers calorimeter, occasioned by errors occurring under conditions of high temperatures and low humidities, has been made by Richford,<sup>413</sup> who presents new charts and graphs for calorimeter corrections particularly applicable to high B.t.u. natural gas.

As a part of the 1935 Production Committee Report of the Pacific Coast Gas Association, White<sup>414</sup> has offered a scheme for a rapid systematic qualitative analysis for metallic ions employing the microscopic identification of crystal forms, as well as certain non-microscopic identifications. The procedure is detailed and the crystal forms obtained illustrated by photomicrographs.

Trials have been made of the photoelectric cell for the measurement of the haze density of combustion gases,<sup>415</sup> such as water gas blast gas.

**Chemical Engineering Processes.** Among the papers of interest in connection with the chemical engineering phases of the production of gaseous fuels are those of Brown and co-workers,<sup>416</sup> of Carey, Griswold, McAdams, and Lewis<sup>417</sup> on plate efficiencies in the rectification of binary mixtures, and of Holbrook and Baker on the entrainment in bubble cap distillation towers.<sup>418</sup>

The course of liquor flow in packed towers has been studied by Chilton, Vernon, and Baker.<sup>419</sup>

Of considerable interest are the efforts of Colburn<sup>420</sup> and of Chilton and Colburn<sup>421</sup> to correlate data on convective heat transfer, fluid friction, and absorption in such a manner as to permit the prediction of one from the other.

The practical usefulness of the Reynolds number in the calculation of the flow of fluids has been extended through the classification of pipe roughness and the establishment of friction factors for such classes of roughness by Pigott<sup>422</sup> and Kemler.<sup>423</sup>

The protection of gas plant equipment against corrosion has been given some attention. Thus, Korany and Bliss<sup>424</sup> report on a tubular condenser in which the corrosion was reduced by 98.8 percent, by the use of the Kirkaldy system in which the system is made cathodic through the use of 5 amperes d.c. per 1000 cubic feet of cooling surface, the anodes consisting of stout iron bars arranged near the side walls.

Colburn and Hougen<sup>425</sup> have outlined a method for the computation of condenser surfaces and call attention to possible improvements in operations through the use of higher gas and water velocities.

Other papers of interest relating to unit processes are those on the diffusion of vapors through gas films by Sherwood and Gilliland,<sup>426</sup> on the film concept in petroleum refining by Monrad,<sup>427</sup> and of Fenske, Tongberg, and Quiggle<sup>428</sup> on packing materials for fractionating towers.

Van der Pyl<sup>255</sup> has outlined recent developments in the flow of fluids. Huff and Logan,<sup>429</sup> in reviewing the status of gas engineering flow formulas, present a method for determining the flow of gas applying the Reynolds number in a form convenient for computation and include an alignment chart illustrating the method.

A review of solution cycles, including such processes as those of Koenemann for generating high pressure steam by the use of exhaust steam, has been given by Sellow.<sup>430</sup>

The writers are indebted to the several members of the Department of Gas Engineering who aided in assembling the material used in the preparation of this chapter.

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## Chapter XIX.

# Petroleum Chemistry and Technology.

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**General and Economic Developments.** Petroleum still continues to be big business. The annual gasoline bill is estimated at 2.5 billion dollars and the oil bill at 250 million dollars.<sup>1</sup> Gasoline consumption is about 16.5 billion gallons per year<sup>2</sup> and it is estimated that two million dollars per day is paid by the American gasoline consumer for taxes over and above the cost of the motor fuel. While Diesel fuels are hardly known to the average consumer, 31 states already have a tax on Diesel fuels ranging from 2 to 6.5 cents per gallon.<sup>3</sup> It is also estimated that there are some 925,000 more cars, trucks and busses on the roads today than a year ago. This alone requires an additional 13 million barrels of gasoline.<sup>4</sup> The use of fuel oil is also extending. The new S. S. Normandie consumes a minimum of some 60,000 barrels of fuel oil on a round trip from Europe to the United States.

During the year the oil business was confronted with various European nationalistic policies, as well as legislation and government control problems at home. Despite all this there has been a general increased development and construction throughout the industry, involving additional investments of many million dollars. A survey of the supply of petroleum has been made and methods for increased conservation outlined.<sup>5</sup> Conservation is also being effected through better control of evaporation losses.<sup>6</sup>

**Production.** There has been increased production activity throughout all the oil-producing states. Geophysical prospecting methods have caused increased drilling operations, not only in new areas but also deeper drilling is being resorted to in old areas.<sup>7-10</sup> Daily production of crude oil in 1935 is estimated to be about 2.7 million barrels per day higher than in 1934. Texas is the largest producer, with California and Oklahoma next in order. The total crude oil produced in the United States up to 1935 is 16.6 billion barrels, while crude production for the first six months in 1935 was 473 million barrels.<sup>11, 12</sup> During the first six months of 1935 there were 10,329 wells drilled; 71 percent of these were oil wells, 22 percent were dry wells, and 6 percent were gas wells.<sup>13</sup> In California there were more wells drilled in the first nine months of 1935 than in all of 1934. The Rodessa field in Louisiana, opened this year, has an initial potential production esti-

mated at 25,000 barrels per day<sup>14, 15</sup> while in the Michigan field, in which there was increased activity, a peak production of 50,000 barrels per day was reached. The output of the Michigan field for the first nine months of 1935 is estimated at 11,190,000 barrels.<sup>16</sup> In Pennsylvania there have been several large gas wells discovered, having an estimated production of several million or more cubic feet of gas per day.<sup>17-19</sup> The deepest oil well, in Upton County, Texas,<sup>20</sup> is now at 12,786 feet and there are many wells producing at the 8000 to 10,000 foot level.<sup>21</sup> Water flooding is being applied with greater care in the East Texas<sup>22</sup> and Mid Continent areas.<sup>23</sup> Oil sands, as well as limestone formations, may respond to proper acid treatment, and under favorable conditions the production of wells may increase one hundred or more percent by treating with hydrochloric acid.<sup>24</sup>

**Corrosion and Construction Materials.** Large quantities of material are needed to replace those rendered useless by corrosion. In underground pipe lines cathodic protection is stated to be practical, and if power from a mechanical source is not available, the installation of zinc anodes is recommended.<sup>25</sup> As a means for generating power for this type of protection, wind mill electric current generators have been placed along pipe lines.<sup>26-28</sup> Corrosion inside pipe lines from sour crudes is also a problem. It may be reduced by removing either the water or hydrogen sulfide or both from the crude, but at present there is no economical method for hydrogen sulfide removal.<sup>29</sup> In refining equipment the use of alloy steels is steadily being extended.<sup>30</sup> Chromium, nickel, and molybdenum steels are used in distillation and cracking equipment.<sup>31, 32</sup> At low temperatures, such as those encountered in vaporizing propane, which is being used in lubricating oil manufacture, ordinary steels have been found to have an unsatisfactory impact resistance, so that unnecessary hazards are encountered. Certain solid solution types of alloys as the austenitic chrome-nickel steels and copper alloys seem more satisfactory for this purpose, and there are encouraging possibilities in the manganese-silicon steels.<sup>33</sup> In producing operations alloy steels are used extensively.<sup>34</sup>

**Low Molecular Weight Paraffins.** There has been a considerable amount of new information reported on the normally gaseous paraffins during the year. Natural gas has been fractionally distilled in a commercial way to yield relatively pure fractions of methane, ethane, propane, or butane. In producing ethane, the fractionating column may be operated at a pressure as high as 1500 pounds per square inch; temperatures as low as  $-100^{\circ}$  F. are also obtainable by using liquid propane as the cooling agent in the condenser. In one plant capacities of the order of 2 million cubic feet per day are planned.<sup>35, 36</sup> Uses for the readily liquefiable hydrocarbons, such as propane and butane, are increasing. These gases are used for cooking, water heating, and refrigeration in homes, camps and towns not served by natural or manufactured gas. They are also being used for motor fuels, and industrially in glass making, steel treating, pottery manufacture, oxy-



propane cutting of iron and steel, lubricating oil manufacture, and for heating orchards and greenhouses. It is reported that these gases, used in special heaters in greenhouses, give a phenomenal growth to plants, because the combustion products, carbon dioxide and water vapor, saturate the atmosphere and stimulate a rapid growth of vegetation.<sup>37, 38</sup>

A summary has been made of the thermal reactions or pyrolysis of the gaseous paraffin, olefin, acetylene, and cycloparaffin hydrocarbons.<sup>39</sup> The thermal decomposition of methane, ethane, propane, butane, and the corresponding olefins have been studied from the viewpoint of maximum olefin and liquid fuel production. Propane was studied in detail and the removal of hydrogen from the gas mixture by selective oxidation is reported.<sup>40</sup> Acetylene has been obtained by pyrolyzing methane, ethane, propane, butane, and isobutane at temperatures of 1100 to 1400° C.<sup>41</sup> Under optimum conditions in KA2S steel tubes, it was possible to convert 74 percent and 82 percent by volume, respectively, of ethane and propane into olefins.<sup>42</sup> Propane and butane were pyrolyzed at 725 pounds per square inch and 550 to 575° F., yielding a gas containing lower molecular weight paraffin and olefin hydrocarbons, as well as a liquid product. By subsequently polymerizing the olefins to liquids it was thought that upwards of 10 gallons of liquid fuel per 1000 cubic feet of commercial butane might be produced.<sup>43</sup> The primary decomposition products of propane in the presence of water vapor may be accounted for by three reactions: (1) dehydration, (2) demethanation, and (3) a bimolecular decomposition into propylene, ethane, and methane. Water vapor is substantially an inert gas up to 700° F.<sup>44</sup> The primary decomposition of pentane appears to be a first order reaction at 600° C. Increase of dilution with steam decreases the amount of ethane and increases the amount of ethylene and hydrogen formed.<sup>45</sup>

The chlorination of propane, butane, isobutane, pentane, and isopentane was studied; it was found that carbon skeleton rearrangements do not occur during either photochemical or thermal chlorination, if pyrolysis temperatures are avoided. Every possible monochloride derivable without such rearrangement is always formed. This generalization also applies to the polychlorides so far as studied.<sup>46</sup> Further work has given a method for calculating from the structural formula of any paraffin hydrocarbon, the percent of its various isomeric monochlorides obtainable by noncatalytic chlorination at temperatures from -65 to 600° C.<sup>47</sup>

The nitration of paraffin hydrocarbons with less than six carbon atoms has been accomplished in the vapor phase. Hydrocarbon vapors were passed through concentrated nitric acid at 108° C. and the resulting mixture of about 2:1 molal ratio of hydrocarbon to nitric acid, was passed through a tube at temperatures from 150 to 420° C. Possible uses for these nitro compounds are: (1) primary compounds for Diesel fuels, (2) raw materials for synthesizing such products as aldehydes,

ketones, amines, nitro-alcohols, nitro-olefins, amino-alcohols, and fatty acids; (3) refining solvents for lubricating oils, and (4) lacquer solvents.<sup>48</sup>

The formation of alicyclic hydrocarbons from free radicals was studied by decomposing diheptyl mercury at about 350° C. Cyclohexane and some unidentified cyclic products were obtained. It appears that the cyclohexane was produced by direct decomposition of the heptyl radical rather than through some polymerization process of ethylene.<sup>49</sup>

**Low Molecular Weight Unsaturated Hydrocarbons.** It is estimated that some three hundred billion cubic feet of gas are produced yearly by cracking processes. This gas contains a considerable quantity of olefin hydrocarbons. Utilization of the gas is, in general, developing along two lines; (1) chemical utilization, as evidenced by the placing in operation of the ten million dollar plant of the Carbide and Carbon Chemicals Co. at Whiting, Indiana, using these gases as raw materials, and (2) polymerization into hydrocarbon fuels by the refiners themselves. The industrial significance of this latter development will be outlined under motor fuels. Other than the cracked gas itself the cheapest raw material for producing olefins is gas oil. New data are available on cracking this material primarily for olefin production at temperatures higher than those used in gasoline production. The effect of pressure in promoting the absorption of ethylene in sulfuric acid is reported, and the formation of ethyl ether by reaction of diethyl sulfate and ethyl alcohol has been reviewed.<sup>50</sup> The reactions of the simpler acetylenic hydrocarbons, such as monovinylacetylene and its polymers, which lead to the preparation of synthetic rubber, have been reported.<sup>51</sup> Cheap acetylene is one of the principle factors in cheap synthetic rubber, or DuPrene, and methods for producing it have been studied. Acetylene is formed by pyrolyzing ethylene, propylene and 1-butene at temperatures of 1100 to 1400° C. with fractions of a second time of contact. Under these conditions over half the decomposition may take place to yield acetylene.<sup>52</sup>

The polymerization of olefins has been studied rather extensively. The kinetics of ethylene polymerization were studied particularly for the purpose of obtaining more information on the effect of minute traces of oxygen on the rate of polymerization, the temperature coefficient of the reaction, and the character of the primary products formed.<sup>53</sup> Under optimum conditions the polymerization of pure ethylene and propylene may give yields of liquid polymer amounting from 70 to 80 percent from ethylene, and from 60 to 65 percent from propylene. Polymerization of these two hydrocarbons was studied over the pressure range 500 to 3000 pounds per square inch and at temperatures from 650 to 850° F. Octane numbers of the liquid polymer are also reported.<sup>42</sup> Polymerization of olefins in the presence of 90 percent phosphoric acid gives a mixture of paraffinic, olefinic, naphthenic and aromatic hydrocarbons. The high pressure catalytic polymerization of ethylene gives isobutane, the percent increasing with increasing tem-

perature of polymerization. From 250 to 330° C. it varies from 2.5 to 18.8 percent by weight of the ethylene that reacted.<sup>54</sup> The mechanism of olefin polymerization by catalysts such as boron fluoride, aluminum and zinc chlorides, phosphoric acid, alumina, and silica gel has been discussed.<sup>55</sup> Propylene polymerized by liquid phosphoric acid at 135 to 200° C. and 1 to 15 atmospheres pressure yields a mixture of mono-olefins. A mechanism for the reaction is suggested, involving the formation of intermediate esters.<sup>56</sup> Isomeric butylenes are similarly polymerized by phosphoric acid, isobutylene polymerizing the most readily and  $\alpha$ -butylene the least. The presence of isobutylene has been found to accelerate the polymerization of the *n*-butylenes.<sup>57</sup> Polymerization of propylene by aluminum silicate catalysts at atmospheric pressure and 350° C. yields a mixture of five-, six-, seven-, eight-, and nine-carbon hydrocarbons, with olefins predominating. Pentenes are the lowest boiling product of the polymerization and consist principally of trimethylethylene. The dipropylenes formed are 2-methyl-2-pentene, and tetramethylethylene; 2-methylpentane is also formed.<sup>58</sup>

Condensation reactions involving olefins have also been reported during the past year. Olefins and paraffins have been found to react in the presence of boron fluoride gas, finely divided nickel, and a small amount of water. The reaction consists of the alkylation of the paraffin to higher molecular weight paraffins through the addition of one, two, or more olefin molecules. The paraffins alkylated so far contained a tertiary carbon atom. Attempts to alkylate *n*-paraffins, such as pentane, propane, and methane with boron fluoride, were not successful. *n*-Paraffins, with the possible exception of methane and ethane, can be alkylated in the presence of aluminum or zirconium halides.<sup>59</sup> Naphthenic hydrocarbons and olefins have been condensed. Cyclohexane, methylcyclohexane, and methylisopropylcyclohexane have been alkylated by ethylene in the presence of aluminum chloride. Boron fluoride catalyzes the alkylation of methylcyclopentane and methylcyclohexane with ethylene.<sup>60</sup> The direct alkylation of aromatic hydrocarbons is reported by periodically introducing ethylene at 250° C. under pressure into a stirred mixture of 10 mols. of benzene, 50 grams of phosphorus pentoxide, 24 grams of lampblack and 10 grams of cresol, to form mono- and hexaethylbenzenes. In a similar way, benzene and isobutylene, toluene and propylene, and naphthalene and ethylene were alkylated.<sup>61</sup> Using 85 percent phosphoric acid, the direct alkylation of benzene, naphthalene, and tetrahydronaphthalene with ethylene at 300° C. was obtained; similarly alkylation of naphthalene and fluorene by propylene occurred at 200° C.<sup>62</sup> The mono-, di-, tri-, and tetraiso-propyl derivatives of benzene were prepared by condensing propylene with benzene, employing boron fluoride. Aluminum chloride promotes the formation of *m*-diisopropylbenzene, while boron fluoride gives the *p*-diisopropylbenzene.<sup>63</sup> The addition of sulfur dioxide to methylpropene, 1-pentene, 2-pentene, 1-nonene, 3-cyclohexylpropene, and 3-methylcyclohexene yields polysulfones. These are neutral products and the

first five of them have alcohol groups at the ends of the chains. The molecular weights of these polysulfones are in the range of 100,000 to 200,000.<sup>64</sup>

The limits of inflammability of ethylene in air and in oxygen were determined as volume percent and found to be for air, lower limit 2.75 percent, and upper limit 28.6 percent; for ethylene in oxygen, lower limit 2.9 percent and upper limit 79.9 percent.<sup>65</sup>

**Physical Data.** The properties of methane in hydrocarbon oils have been studied,<sup>66</sup> as well as the viscosity of methane and propane solutions in hydrocarbon oils at various pressures and temperatures.<sup>67</sup> The physical constants of propane have been summarized<sup>68</sup> and specific heat data for propane and butane in the range of 60 to 220° F. are reported.<sup>69</sup> The heat of combustion of isobutane, forming gaseous carbon dioxide and liquid water at 25° C. and one atmosphere pressure, was found to be  $686.3 \pm 0.13$  kilocalories per mole. It was calculated that at 25° C. the internal energy of isobutane is less than that of butane by  $1.63 \pm 0.15$  kilocalories per mole.<sup>70</sup> A temperature-entropy diagram, specific gravity as a function of pressure and temperature, and pressure-fugacity ratios are now available for pentane.<sup>71</sup> The effect of pressure on the isothermal change in heat content for pentane was calculated and found to agree with experimentally determined values. The effect of pressure on the heat content (enthalpy) of benzene has been experimentally determined and used for the construction of an enthalpy-pressure-temperature chart.<sup>72</sup> The properties of 1-octadecene, octadecane, di-*m*-tolylethane,<sup>73</sup> and tetratriacontadiene ( $C_{34}H_{66}$ ) have been measured.<sup>74</sup> Variations in hydrocarbon structure have been correlated with spontaneous ignition temperatures. It has been found that, for the same number of carbon atoms, the spontaneous ignition temperature falls roughly in the order, aromatics, alkylated aromatics, naphthenes, alkylated naphthenes, straight chain paraffins, branched chain paraffins, and unsaturated aliphatics.<sup>75</sup> Molecular weights by the cryoscopic method are reported for various Mid Continent cracked gas oils and pressure still charging stocks. Molecular weights have been correlated with boiling point, viscosity, and density to enable an estimation of the molecular weight of any given cracked stock to be made.<sup>76</sup> High temperature viscosities of liquid petroleum fractions have been measured over the range 100 to 800° F., and from atmospheric to 500 pounds per square inch.<sup>77</sup>

**Internal Combustion Engine Fuels.** Tests on a large number of cars in the New England and Eastern states showed that from 5 to 6 percent of the passenger compartments contained dangerous proportions of carbon monoxide. A person breathing air containing 8 parts of carbon monoxide per 10,000 of air would probably experience headache, impaired judgment and decreased mental alertness in about 1 hour, collapse in about 1.5 hours, and death in about 2 hours if not removed from the poisoned atmosphere.<sup>78</sup> This is important in view of the increased use of automotive power. Busses are steadily

replacing street cars, because motor bus transportation synchronizes with all other forms of motor traffic present today on streets and highways.<sup>79</sup> The use of Diesel-electric drives on railroads is also increasing.

Regarding air-fuel ratio in automotive engines, the maximum thermal efficiency is found at about 16 to 1, the highest mean effective pressure or torque at 12.5 to 1, and the maximum economy at about 14 to 1. Experiments have shown that 6.4 percent more gasoline is used with S.A.E. 60 oil than with S.A.E. 30 oil, and 3 percent more for S.A.E. 30 than for 10-W, in consequence of higher friction.<sup>80</sup> Furthermore, compilation of results obtained on 213 automobiles and trucks and 184 busses used by the Milwaukee Electric Railway and Light Company shows that gasoline consumption of vehicles reasonably well maintained, does not depend on the age of the vehicles or the miles from overhaul or piston ring change, is influenced greatly by carburetor conditions, proper jets, proper float level, choke operation and freedom from leaks; increases greatly as the number of starts and stops increases, depends on loads carried, is influenced by average daily mileage, is influenced by temperature and weather conditions, is adversely affected by very fast schedules, and is affected adversely if the gasoline is too volatile.<sup>81</sup> The ten, fifty, and ninety percent distillation points on the gasoline distillation curve are now lower than for any previous year,<sup>82</sup> and there have been several studies made on gasoline volatility.<sup>83-85</sup>

Propane and butane have been used alone as motor fuels. There are two advantages claimed, namely, high octane number—125 for propane and 93 for butane—and high volatility, ensuring good distribution to the cylinders. A compression ratio of 10 to 1 is reported possible with propane, and 7 to 1 with butane, if the engine is of sufficiently rugged construction. However, the power produced, as well as the fuel consumption in terms of B.t.u., are found to be nearly the same as when gasoline is burned. This is explained by the cooling effect of the liquid gasoline vaporizing in the cylinder. From the standpoint of supply, availability, cost of distribution, and price, the general replacement of gasoline as an automotive fuel with liquefied petroleum gases is not economical. However, use will likely be found in large high powered stationary engines, in rail cars and trains, and in switching, tunnel, and construction engines.<sup>86-88</sup>

There has been marked activity throughout the petroleum industry to make commercially available a high octane number fuel, i. e., one of the order of 100 octane number. The demand for such a fuel comes practically entirely from the aviation field, where fuel costs are reckoned on the basis of cost per ton mile of pay load rather than cost per gallon. It has been pointed out that if a fuel of extremely high anti knock were available, the cost per ton mile may be lower even if the cost of the gasoline were doubled. The result is that a technical grade of isooctane or 2,2,4-trimethylpentane, has been made available and a considerable quantity has been ordered by the U. S. Army for

experiments on increase in engine power without a corresponding rise in weight. Gasoline of such high anti knock quality permits further increases in the supercharging of aircraft engines, thus increasing overall performance, the ease and safety of take-offs, and a quicker pick-up in emergencies. It further permits increases in compression ratio with a resultant decrease in fuel consumption. This is of particular importance for military long distance bombers, and for commercial transports where long non-stop flights are made. Now that the successful non-passenger flights of the Pan American clipper ship to Hawaii, Midway, and Wake Islands and the Philippines have been realized, there is considerable need for higher octane number fuels that would permit even relatively small decreases in fuel consumption, for on these long trans-Pacific flights this would permit a substantial increase in the passenger load. It was hoped that the gasoline resulting from polymerizing the olefins in cracked gases would be this unusually high octane number fuel. While polymer gasoline has a knock rating of 80 octane number or better, it does not as yet appear that it will be the much sought for 100 octane number fuel. Furthermore, while the addition of lead tetraethyl to isooctane affords even additional significant increases in the highest useful compression ratio and consequently in power and output, the polymer gasoline appears to have the characteristic of not responding very well to lead tetraethyl additions. That is, octane number does not rise nearly so fast as in the case of isooctane upon the addition of lead tetraethyl.<sup>89-92</sup>

It is estimated that if, throughout the United States, the olefins present in cracked gases were polymerized, there would be available an additional 30 million barrels of polymer gasoline, or about 7 percent more gasoline than is now being produced.<sup>93</sup> There are already plants in operation having capacities of the order of one thousand barrels of polymer gasoline per day. In general, the polymerization of these olefins occurs in one of two ways: (1) at relatively low temperatures in the presence of catalysts, or (2) at elevated pressures and temperatures in the absence of catalysts. In the catalytic method, the operation is reported as taking place at about 400° F. at pressures of 175 to 200 pounds per sq. in. in the presence of a phosphoric acid type catalyst. Yields of from 2.5 to 10 gallons of an 80 octane number gasoline per 1000 cubic feet of gas are reported.<sup>94, 95</sup> In one type of non-catalytic polymerization, operating conditions are about 1000° F., and 800 to 1000 pounds per sq. in.<sup>96, 97</sup> while in another operation the temperatures are higher, namely 1150 to 1300° F., and the pressures 50 to 75 pounds per sq. in. It is reported that under these latter conditions complete rearrangement of the molecules occurs, giving cyclic as well as aromatic hydrocarbons such as benzene, toluene, xylene, and naphthalene.<sup>93, 98, 99</sup>

The use of alcohol for addition to gasoline has continued to be discussed. It is claimed that the farmers consume some 23 percent of the gasoline in the United States and that the addition of 10 percent

alcohol would create a market for 1.6 billion gallons of alcohol a year. This procedure is reported to be unsound in this country at present, for it is claimed that the fuel consumption of a 10 percent alcohol blend is about five percent higher than straight gasoline, and the consumer would likely pay more for this fuel.<sup>100-103</sup>

The addition agents for gasoline at present consist of one or more of the following types of materials: (1) halogenated hydrocarbons reported to minimize carbon troubles in engines,<sup>104</sup> (2) antioxidants or gum inhibitors, (3) top cylinder lubricants, (4) color stabilizers such as the aliphatic amines of less than 5 carbon atoms,<sup>105</sup> and (5) lead tetraethyl as an anti knock addition agent. Iron pentacarbonyl has the ability to suppress knock. It is reported that 3 cc. per gallon can raise the octane number from 58 to 96, but that the compound is so unstable to both light and air that it is nowhere in commercial use. A long literature and patent bibliography is available for iron carbonyl.<sup>106</sup>

Diesel fuel standards are desired which will include ignition quality, viscosity, gravity, distillation characteristics, cleanliness, Conradson carbon, ash, sulfur and corrosion acids, flash point, and pour point.<sup>107</sup>

**Gasoline Preparation and Manufacture.** In connection with the American Petroleum Institute Project No. 6 at the National Bureau of Standards, it is reported that in the 55 to 145° C. fraction of a Mid Continent gasoline there have now been isolated: (1) the normal paraffins, hexane, heptane, and octane; (2) the 2-methyl derivatives of these normal paraffins; (3) the hexane isomers, 2,3-dimethylbutane and 3-methylpentane; (4) methylcyclopentane and methylcyclohexane; (5) the aromatics, benzene, toluene, ethylbenzene, and the three xylenes. The hydrocarbons now isolated account for about two thirds of the entire volume boiling between 55 and 145° C. The paraffins, naphthenes, and aromatics boiling in this range are present in about the proportion 6:3:1. In the fraction boiling between 145 and 180° C., nonane was present to the extent of 15.5 percent, decane 12.5 percent, mesitylene 0.3 percent, pseudocumene, 3.0 percent, hemimellitene 0.9 percent. It is very likely that this fraction will yield far less than the total of 80 compounds reported in the literature as boiling within these limits.<sup>108, 109</sup> The separation of aromatic and olefin hydrocarbons from paraffins and naphthenes by means of adsorption on silica gel is reported.<sup>110</sup> A procedure has been outlined for the classification of hydrocarbons depending upon grouping according to physical constants, as well as on standardized chemical reactions.<sup>111</sup>

In the natural gasoline field, there are over 1,000 plants in operation in the United States producing about 10 million gallons of natural gasoline per day. About 200 of these plants are in Oklahoma, and about 130 plants are in each of the following states: Texas, Pennsylvania, and California.<sup>112, 113</sup> In view of the importance of natural gasoline to the overall volatility of motor fuels in general, an index for fuel volatility has been proposed in which the variables of engine

performance, atmospheric temperature, starting, and fuel efficiency are considered.<sup>114</sup>

The effectiveness of lead tetraethyl in different hydrocarbons has been studied. Quantitative measurements were made of the specific anti knock effect of lead tetraethyl in 62 different hydrocarbons, by finding the increase in critical compression ratio, in a single-cylinder-variable-compression engine, made possible by the addition of one cc. per gallon of lead tetraethyl. On this basis there are variations of as much as twenty-fold in the effectiveness of lead tetraethyl in suppressing knock in different hydrocarbons.<sup>115</sup> It has also been found that the various sulfur compounds in gasoline affect the lead susceptibility of the gasolines.<sup>116</sup> For the removal of sulfur compounds from gasoline, treatment with solutions of copper salts has been found to be economical.<sup>117</sup>

Increasing amounts of valuable data on distillation equipment design are available.<sup>118-120</sup> A single distillation tower now produces five products from crude oil at the rate of 17,000 barrels per day.<sup>121</sup> Factors affecting entrainment in bubble cap columns have been studied<sup>122</sup> and an outline of the primary distillation applications in the petroleum industry has been made, together with design data for gas recovery and stabilization systems, and gasoline and lubricating oil manufacture.<sup>123</sup>

Cracking operations are now on a highly developed scale. Single units combining the processes of cracking, skimming, reforming, and stabilization are in operation resulting in greatly reduced manufacturing costs.<sup>124</sup> The largest combined distillation and cracking unit is the new plant at Texas City, Texas, of the Pan American Petroleum Corporation. The daily charging capacity is 35,000 barrels of crude oil. Long time cracking runs of 98 and 123 days have been reported.<sup>125, 126</sup> The various factors in cracking such as time, temperature, pressure, and conversion per pass through the apparatus have been studied.<sup>127</sup> Experimental cracking apparatus has been worked out for giving data applicable to plant design, such as yields of gas, gasoline, coke and polymers as a function of time, temperature, and pressure. Specific volume data are also available as a function of time, temperature, and pressure. As a result of these data a new basis has been found for the design of cracking plants.<sup>128</sup> A correlation of plant cracking data has been obtained that satisfactorily gives the octane number obtainable in reforming naphtha in terms of the octane number of the charge and the amount of cracking to which it has been subjected.<sup>129</sup>

Antioxidants and gum inhibitors are now used extensively to prevent gasoline deterioration and eliminate the necessity for acid refining. These products are daily applied to more than five million gallons of gasolines, resulting in annual savings of millions of dollars. The critical oxidation potential of inhibitors has been studied with regard to the induction period afforded cracked gasolines.<sup>130</sup> It has been found that gum formed by oxidized gasolines is high in peroxides, aldehydes,



and acids. It appears that peroxides are the substances primarily responsible for gums.<sup>131</sup>

Standardized tests for gasoline color stability have been reported,<sup>132, 133</sup> as well as a potentiometric method for the determination of mercaptans.<sup>134</sup> Improvements in the A.S.T.M. lamp method for sulfur have also been suggested.<sup>135</sup>

**Lubricating Oil Preparation and Manufacture.** Improvements in lubricating oil preparation have been principally in solvent extraction processes, and in addition agents such as pour point depressors, oiliness or lubricity carriers, extreme pressure materials, anti-oxidants, and viscosity index improvers. A new addition compound for lubricating oils, methyl  $\alpha,\alpha$ -dichlorostearate, is being used.<sup>136</sup>

Solvent extraction of lubricating oils consists essentially of a suitable mixer or tower wherein oil and solvent are contacted as two liquid phases, distillation equipment to separate solvent from these phases for reuse, i. e., a solvent recovery system, the further processing of the insoluble oil, or raffinate, to make finished lubricating oil, and the disposal of the dissolved oil or extract. At present the following solvents are in industrial use in refining lubricating oils: sulfur dioxide, nitrobenzene, benzene-acetone-toluene mixtures,<sup>137</sup> ethylene dichloride and benzene, dichloroethyl ether,<sup>138</sup> propane and cresylic acid,<sup>139</sup> furfural,<sup>140</sup> phenol,<sup>141</sup> propane<sup>142, 143</sup> and aniline,<sup>144, 145</sup> A graphical method, employing triangular coordinates for representing equilibrium in complex oil-solvents systems, has been developed as a basis for the solvent refining of oils. Calculations using data obtained in nitrobenzene extraction are given.<sup>146</sup> The decolorization of lubricating oils by percolation through earths has been studied.<sup>147</sup>

A means for characterizing petroleum fractions is reported, employing empirically developed charts and the factors of specific gravity, boiling point, viscosity, aniline point, viscosity index, and hydrogen content. These determinations enable the predictions of other properties with fair approximation for engineering use.<sup>148</sup> Another correlation of viscosity, gravity, and S.A.E. classification has been made.<sup>149</sup>

**Performance and Testing of Lubricants.** It is stated that oil consumption can be controlled by using the minimum practical clearance between pistons and cylinder walls, by providing large oil return capacity in oil return rings, piston oil holes, and passages, by designing pistons so they are round when hot, by replacing rings when they are badly worn or when the oil return grooves are clogged, by using expanders in back of piston rings in worn cylinders, by maintaining correct main bearing clearances, and by preventing excessive crank-case temperatures.<sup>81</sup> The effect of viscosity and volatility on oil consumption, and of cylinder carbon on knock has also been reported.<sup>150</sup> During the year there have been several laboratory testing machines described for testing the ordinary as well as the extreme pressure characteristics of oils.<sup>151, 152</sup> Improvements have been made in apparatus for accurately determining the kinematic viscosities of oils

at various temperatures,<sup>153</sup> and conversion tables have been formulated on the basis of experimental data giving the relationship between kinematic viscosity and Saybolt Universal Seconds.<sup>154</sup> A boiling point-gravity constant is proposed as an index of lubricating oil characteristics.<sup>155</sup> Improved viscosity index tables are available for calculation in terms of kinematic viscosity as well as Saybolt Seconds.<sup>156</sup>

Bearing corrosion has placed additional problems on the refiner of lubricating oils. It has been found that excessive oil temperatures with oils which have been made to resist oxidation, and which are considered to be of the highest quality, appear to corrode the new bearing metals, such as cadmium-nickel, cadmium-copper, or copper-lead alloys. It is believed that this is due principally to excessively high oil temperatures, and that these temperatures should be kept below 250° F.<sup>157, 158</sup> It has also been found that different types of extreme-pressure lubricants should not be mixed in automobiles. Most extreme-pressure lubricants contain one or more of the following elements in one combination or another: lead, sodium, aluminum, chlorine, and sulfur. In addition other materials may possibly be used such as castor oil, lard oil, and glycerin. Lead may therefore react under proper conditions with sulfur or chlorine to give insoluble sulfides or chlorides, and these are no part whatever of extreme-pressure lubricants. In other ways, mixing of different extreme-pressure lubricants may cause foaming, thickening, sludge, or other undesirable results.<sup>159</sup>

Improvements in greases have been in the direction of avoiding acidity and consequent bearing corrosion, avoiding hydrolysis of greases, and decomposition due to a change in the degree of dispersion of the soaps.<sup>160, 161</sup> Laboratory service testing methods of automotive lubricating greases have been outlined, and the best methods for correlation with actual service performance tests have been studied.<sup>162</sup> The fine structures of lubricating greases have been examined by a dark field microscope technique, and the suggestion has been made that a useful classification of greases would result, depending on the length of the soap fibers, where the fiber length varies from 0.001 mm. to 0.080 mm.<sup>163</sup>

**Miscellaneous Developments.** A system to evaluate the susceptibility of asphalts to temperature change has been used similar to the viscosity index system for lubricating oils. Asphalts from heavy Mexican crude have been used as the basis for the 100 index material, while petroleum tar from cracking served as the basis for the zero index. Results using this method on various straight reduced asphalts have been tabulated.<sup>164</sup> The oxidation of the constituents of asphalts has also been studied. It is believed that through oxidation unstable compounds form, from which carbon dioxide and water are eliminated, leaving residues that polymerize.<sup>165</sup>

Spray oils apparently injure foliage because of the unsaturated hydrocarbons they may contain. Oils containing over 10 percent of unsaturated hydrocarbons may contain injurious quantities of asphalt-

ogenic acids formed from the unsaturated hydrocarbons by oxygen in the presence of light.<sup>166</sup>

The field of petroleum solvents is increasing. A study has been made of the industrial solvents in use. The list contains petroleum solvents, ketones, polyethers, esters, ether-alcohols, alcohols, chlorinated compounds, naval stores solvents and furane derivatives.<sup>167</sup> A modified and improved Kauri butanol test for the solvent power of hydrocarbon solvents has been reported.<sup>168</sup>

The oiling of coal for dust proofing and preventing spontaneous combustion is reported. The oil specifications suggested are 100 to 225 Saybolt viscosity at 100° F., with a flash point of 305 to 370° F. The oil is sprayed onto the coal and it may also be emulsified with water. It is stated that in the ordinary method of water-wetting coal, the consumer loses in two ways: (1) by substituted weight and (2) by a loss in heat units required to vaporize the water.<sup>169</sup> There is also a need for standardization in fuel oil burners for household heating. Several billion barrels of fuel oil are consumed per year and it is becoming desirable to standardize on one or two grades instead of the many types now existing.<sup>170</sup>

Over 300 million pounds of carbon black are now made yearly. The yield from natural gas is about 1.4 pounds per thousand cubic feet of gas. Over half the production goes into rubber manufacture; the remainder goes into inks, paints, and other miscellaneous uses.<sup>171</sup>

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## Chapter XX.

### Detergents and Detergency.

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The term detergent is derived from the Latin verb *detergere*, which means "to wipe away, or wash away, or cleanse." Agents used for this purpose in daily life and in industry are so numerous that it is difficult to classify them, and the present chapter will be devoted to a few of the more common types only. These will be classed in the following groups: soaps, and similar detergents, soap builders, dispersing compounds for hard waters, enzymes, and bleaches.

This presentation includes chiefly the development of detergents during the past few years, with emphasis on the progress made during 1935. Methods of measuring detergency efficiencies and theories concerning the action of the more common detergents will be included also. The chapter will be confined to the work of American investigators, except in cases in which foreign work needs to be cited in order to make American contributions understandable.

For many years, the term soap has been used almost exclusively for the sodium and potassium salts of the higher fatty acids. The more recent introduction of detergents which serve the same general purpose as these older soaps causes the literature to be somewhat confused as to whether or not the newer soap-like detergents will be classed as soaps. In the laundry and drycleaning industries, in which both of these classes of substances are now used, there seems to be a tendency to refer to the older sodium and potassium fatty acid salts as "soaps," and the newer introductions as "detergents." This presents a problem in nomenclature which is in need of clarification.

An extensive bibliography on launderability has been published by Gugelman,<sup>1</sup> which should prove helpful to everyone in the field. This covers the period from 1910 through 1934.

An interesting history of the soap industry through 1925 was written by Ittner,<sup>2, 3</sup> who recently extended the review to include the last ten years. He points out that there have been no revolutionary changes in soap manufacture during the past few years, although progress has been steady. Improvements have been made in methods of alkali manufacture and of oil and soap production, in effecting a more complete saponification reaction, and in glycerol recovery. Unusual attention has been given to the physical form of soaps, to increase their solubility and convenience in use.

**The New Detergents.** There are many references in the literature to the new detergents which are being substituted in part for the older types of soap. These detergents were introduced to eliminate one of the chief shortcomings of ordinary soap—namely, its tendency to form curdy precipitates in hard waters. The chief difficulty with soaps of the older type is that they are salts of strong bases and weak acids, and hence are unstable in strong acids. Moreover, at ordinary temperature, they form precipitates in hard water by ordinary metathesis of the alkali soaps with any calcium and magnesium compounds which may be present, as follows:  $2 \text{RCO}_2\text{Na} + \text{MgSO}_4 \rightarrow \text{Na}_2\text{SO}_4 + (\text{RCO}_2)_2\text{Mg}$ . At higher temperatures (because the carboxylic acids are weak), these salts hydrolyze more completely as follows:  $(\text{RCO}_2)_2\text{Mg} + 2 \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2 \text{RCO}_2\text{H}$ .

In order to take advantage of the desirable qualities of the ordinary soaps, while eliminating or reducing their shortcomings, various types of new detergents have been prepared. They comprise two main classes of compounds: (1) Acid sulfates of long-chain alcohols; and (2) condensation products of ordinary fatty acids or their derivatives with substances containing a strong acid group.

The first class of detergents is exemplified by compounds of the type of sodium lauryl sulfate, frequently abbreviated as SLS. The second type is illustrated by the Igepons, in which the carboxyl group is "blocked" by condensation with a hydroxy- or an amino-sulfuric acid. The advantages of the introduction of a strongly acid group, such as the  $(-\text{SO}_3\text{H})$  group of the sulfonic acids, or the  $(-\text{OSO}_3\text{H})$  group of the substituted sulfuric acids, depend upon the fact that the sodium salts of compounds containing these groups are more stable in acids than are the salts of weak acids, such as stearic acid and the other members of the fatty acids which are the basis of ordinary soaps. Moreover, the calcium and magnesium salts of sulfated, sulfonated, and similar compounds are more readily soluble than calcium and magnesium soaps.

**Sulfonated and Sulfated Compounds as Detergents.** The *sulfonated oils* are numerous, and include both straight-chain and aromatic compounds. They have a wide application as wetting agents, because they penetrate textile fibers, and are stable in acid solutions. Hence they can be used in dyeing operations in acid solutions, in which soaps are unstable. Most of them form relatively soluble magnesium and calcium salts, and are stable in acid solutions, but they do not meet all of the other requirements for a detergent, in that they are low in dirt removal. Recently there has been introduced a group of sulfated compounds which are good detergents, and which have the other desirable properties of the sulfonated oils. These are now marketed by a number of American firms under various trade names.

**Sulfated Alcohols.** The sulfated alcohols are sulfuric esters of the straight-chain fatty alcohols, containing from 8 to 19 carbon atoms in the chain, and sometimes more. These are produced by a hydrogenation-



tion process, in which high temperatures and pressures cause the hydrogen to react with the carboxyl group in the fatty acid molecule; this reaction reduces the fatty acid either to the alcohol ( $-\text{CH}_2\text{OH}$ ), or to the hydrocarbon ( $-\text{CH}_3$ ) group, according to the temperature, pressure, and other conditions which are maintained during the reaction. This process differs from the older hydrogenation methods, in which relatively low temperatures and pressures were maintained, and in which hydrogen was applied only at the double bond, with no change in other parts of the molecule.

The sulfated alcohols have certain characteristics in common, although they differ from each other in certain properties according to the length of the carbon chains. The lower members of this group of compounds, which are called hymolal salts, are good detergents, while those of the longer chains are poor detergents but good wetting agents.

The following formulas represent the principal components of three representative sulfated alcohols:

- (1) Sodium lauryl sulfate:  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OSO}_3\text{Na}$ .
- (2) Sodium octadecyl sulfate:  $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OSO}_3\text{Na}$ .
- (3) Sodium oleyl sulfate:  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OSO}_3\text{Na}$ .

The first of these is made by hydrogenating coconut or palm kernel oils, which are then fractionally distilled. The sodium salts of these and of similar alcohols are marketed as detergents in this country under such trade names as *gardinol WA*, *Gardinol LS*, *gardinol CA*, *Orvus*, and *Dreft*. These products yield insoluble calcium and magnesium salts below  $100^\circ\text{F}$ . This is not a serious handicap, however, since these salts are soluble at the temperatures most frequently used in washing. The second of the sodium alcohol soaps, for which formulas are given above, has some value as a detergent, but is chiefly useful as a wetting agent. It is made by the high pressure-high temperature hydrogenation of sperm, tallow, or vegetable oils, and can be used satisfactorily only in water solutions above  $130^\circ\text{F}$ ., because its calcium and magnesium salts are insoluble below this point. The third of the salts is made from sperm oil. Products of this range of molecular construction serve chiefly as wetting and finishing agents in textile and allied industries.

The early work on sulfated alcohols was done by many people in different places. Among these should be mentioned H. Berth of the German firm of H. T. Böhme, A. G., who was the first to point out that the carboxyl group in detergents must be eliminated or blocked, for reasons already mentioned. Killeffer<sup>7</sup> presented the following brief discussion of the early history of the high temperature-high pressure hydrogenation reactions to which reference has previously been made: "In 1931 Adkins and Folkers<sup>8</sup> published two papers describing, respectively, the preparation of a hydrogenation catalyst, and the use of this catalyst in the direct hydrogenation of aliphatic acids to the corresponding alcohols having the same number of carbon atoms. Shortly thereafter, Schrauth,

Schenck, and Stickdorn,<sup>9, 10</sup> Deutsche Hydrierwerke, A. G., published a paper describing their method of accomplishing the same result and referring to patent applications previously made by them in Germany in 1928. Normann<sup>11</sup> also published a paper on the process, pointing out the possibility of control of the product (alcohol or ester) by controlling the temperatures. In 1932, a patent was issued in the United States to Lazier<sup>12</sup> describing a similar method of hydrogenation with the rather specific idea of hydrogenating to secure esters simultaneously with the alcohols. Between 1928 and 1931 the commercial development of these fatty alcohol derivatives proceeded abroad and numerous patents were issued to cover them. . . ."

The literature in this country on the sulfated alcohols has become voluminous, and therefore only a few recent contributions will be mentioned. The place of sulfonated and sulfated alcohols in the detergency and textile processing industries was discussed by Harvey<sup>13</sup> at the 1935 meeting of the American Association of Textile Chemists and Colorists. The analytical properties of the commercial sulfated alcohols have been investigated and reported by Biffen and Snell.<sup>14</sup> Sunderland<sup>15</sup> discussed the manufacture, properties and applications of these products in a series of recent articles. Richardson<sup>16</sup> gave some details concerning the manufacture of sulfated alcohols, and stated that in the United States the E. I. du Pont de Nemours and Company and The Proctor and Gamble Company hold licenses from Böhme and Hydrierwerke in Germany for the manufacture and sale of the sulfonated and sulfated alcohols covered by the patents of the latter firms.

**Igepons.** A second group of important new detergents includes the Igepons. These are best known in two forms—Igepon A, and Igepon T. The former is made by producing the sodium salt of a compound formed when isethionic acid combines with oleic acid or its derivatives. It has been found to be a good detergent, neutral in reaction, stable in acids of moderate concentration, but decomposed by strong acids, or on long contact even with weak acids. The term Igepon was coined from the first initials of the German combine which introduced these products—the I. G. Farbenindustrie Akt.-Ges.—the "A" being the first letter of the German word for the acid used in making it—namely, isethionic (German, aethionic) acid.

The lack of stability of Igepon A in alkalies or in strong acids led to the production of Igepon T, the "T" indicating that tauric acid was used in making it. The two Igepons are similar in properties except for the fact that Igepon T is more stable in acid and alkaline solutions. The formulas of these two substances are the following:

Igepon A:  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOCH}_2\text{CH}_2\text{SO}_3\text{Na}$  .

Igepon T:  $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{CON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$

These formulas illustrate the commonly used term "blocking the carboxyl group." In the first instance the hydrogen of the carboxyl

group is replaced by a group which itself contains a polar solubilizing group, while in the second case, the ( $-\text{OH}$ ) of the carboxyl group is similarly replaced.

Sweet<sup>17</sup> discussed the compounds and uses of the Igepons. Lederer<sup>18</sup> described the results of tests on these compounds, which include solubility in water and organic compounds, density of aqueous solutions, viscosity, surface and interfacial tensions, foam number, and foam consistency. Nüsslein<sup>19, 20, 21</sup> described the performance of the Igepons in actual use, and gave a history of their development. In this country, the Igepons are marketed by various firms: Syntex is a trade name for Igepon T sold by Colgate Palmolive Peet, and various Igepons are distributed by General Dyestuffs.

**Miscellaneous New Detergents.** A wide variety of new detergents is being proposed or sold in the United States and abroad, all of which are having some influence on practices in the field of detergency. *Naphthenic compounds*, prepared from the naphthenes recovered from certain petroleum, have been studied and used, chiefly in Russia<sup>22</sup> and Japan.<sup>23</sup> *Sulfonated naphthalene compounds*<sup>24</sup> are marketed as soap substitutes because of their wetting, dissolving, and dispersing properties. A discussion of sulfonated hydrocarbons as detergents is given in Chapter 46 of the recent book by Ellis entitled "The Chemistry of Petroleum Derivatives" (New York, The Chemical Catalogue Company, 1934). Nekal BX, the sodium salt of a naphthalene sulfonic acid with side chains, is an agent of this type. Other products marketed under the trade names "Nekal," "Alkanol," and "Neomerpin N" are substances of similar kind, the latter of which is the free acid instead of the sodium salt. Other agents which assist in soil removal because of their wetting and emulsifying properties have been prepared from related hydrogenated products, such as tetralin.

In some of the new detergents which have been proposed, or actually placed on the market, phosphates or halides have been inserted either as substitutes for the sulfate group, or to increase the polarity of the compound, or for both purposes. Thus, the H. T. Böhme A. G.,<sup>25</sup> in Germany, has patented a wide variety of esters of pyrophosphoric acid with the higher aliphatic alcohols, in which the phosphate groups have replaced the sulfate groups.

The Carbide and Carbon Chemicals Corporation,<sup>26</sup> in America, has patented a cleansing, wetting, impregnating, and emulsifying agent made from methyl isobutyl ketone and ethylhexaldehyde, having this formula  $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_2\text{CHOHCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$ . Baldwin and Davidson,<sup>27</sup> in England have patented a group of ethers produced by the reaction of an alcohol, such as cetyl, dodecyl, or oleyl, with an aliphatic or aralkyl halide, such as benzyl chloride, in the presence of aluminum powder and magnesia or chalk. When heated, and when treated with chlorosulfonic acid, the compounds formed are sulfonated products with good detergent properties.

Calcott and Clarkson<sup>28</sup> have patented a series of detergents of the gen-

eral formula:  $C_n(OH)_{n-1}H_{n+2}NR^1R^2$  where  $n$  is five or six,  $R^1$  is an aliphatic radical having an open chain of at least eight carbon atoms, and  $R^2$  is a hydrogen atom or an aliphatic radical. These compounds are obtained by a process which comprises the reaction of an aliphatic halide having an open chain of at least eight carbon atoms with an amine of the general formula  $C_nH_{n+2}(OH)_{n-1}NXY$ , related to a 5- or 6-carbon sugar. An example of such a compound formed from glucose and lauryl alcohol would have the formula  $C_{12}H_{25}NHCH_2(CHOH)_4CH_2OH$ .

Aliphatic sulfonamides,<sup>29</sup> sulfonated dicarboxylic acids,<sup>30</sup> pine oil preparations, and terpineol sulfate are among the other detergents which have recently been proposed or introduced. Such compounds as phenylphenol sulfate, under such trade names as Aresket, Aresklene, and Areskap, also have been developed.

**Chemical Tests of Detergents.** Space does not permit a complete review of all of the chemical tests for various ingredients in soaps and detergents proposed or used in this country before the close of 1935. Mention should be made, however, of the fact that Hart,<sup>31</sup> acting as Chairman of the Sub-Committee on Sulfonated Oils of the American Association of Textile Chemists and Colorists, reported on tests for sulfonated and sulfated oils during 1935, which indicates that there is increasing interest in reagents of these types in this country.

**Practical Tests for Detergency.** Chemical analysis of a detergent is an insufficient method of evaluating its cleansing properties. An actual washing test is necessary, either in addition to, or instead of, chemical tests. These involve the use of standard soiled and standard white fabrics which possess homogeneity of initial light reflectancy, and which come to have the same final light reflectancy after the same washing treatment. In 1927, the Subcommittee of the American Oil Chemists Society<sup>32</sup> made a report on its work on practical washing tests. In this report, a standard soiled fabric was proposed which consisted of a piece of cotton sheeting which was desized and treated with a soiling mixture of lubricating oil, edible tallow, and lampblack. A method of evaluating the results was proposed, and a machine suitable for making washing tests was described. The method recommended by this Committee evidently was not widely accepted, since we find many investigations with different types of soiled pieces, and different methods of evaluating and reporting results. Thus, Chapin<sup>33</sup> used a cotton fabric soiled with an ointment of lampblack and vaseline, lard, or medicinal oil. He employed a special instrument and evaluated his results by the use of a colorimeter used as a reflectometer.

Rhodes and Brainard<sup>34</sup> measured the detergency of soaps of various concentrations directly under practical laundry conditions. Hill<sup>35</sup> made a study of the comparative performances of various possible constituents of a soiling mixture, and adopted a preparation containing Oildag, olive oil, tallow, and mineral oil. He stated that this contained the chief constituents of general soil, with the exception of albuminous matter. He omitted the latter because it would have made necessary a

relatively low maximum temperature during the experimental procedure. He found that weighing the soiled piece before and after laundering did not give a satisfactory measure of soil removal, and he therefore adopted a photometric method. He used a small agitator type of washing machine in his tests.

Vail<sup>36</sup> stated that the trend in soiling tests was in favor of simple pigments. He described two possible methods of making soiled fabric—one in which umber in a water suspension was applied to a white fabric by passing the fabric back and forth through a clothes wringer, and the other by applying umber in a water suspension in a launderometer.

Morgan<sup>36</sup> described a standard soiled fabric made by the application to desized white cotton of 3 grams of Russian tallow, 10 grams of Nujol, and 2 grams of lampblack, suspended in 2000 c.c. of carbon tetrachloride. Tests were made in a miniature washwheel with results which showed the sensitivity of this fabric. Carter and Stericker<sup>37</sup> used carbon black, burnt umber, and raw umber or ferric oxide as an inert soil in testing the comparative soil-removal values of various soaps and soap builders.

Oesterling and Mack<sup>38</sup> have worked for a number of years on the efficiencies of the standard soiled fabrics described in the literature, and have developed as a result a fabric which now has considerable use in laundry research. This fabric is desized with an amylolytic enzyme, and is soiled in a standard manner with carbon black of definite particle size, motor oil of definite specifications and melted Crisco in a bath of Stoddard solvent. The fabric is treated with the soiling substances in a Stoddard solvent bath, and is rinsed in a Stoddard solvent solution containing Crisco and motor oil of the same concentration as in the soiling bath. The fabric is then dried, washed with soap and water, and rinsed in a definite manner after which it is again dried. Test specimens from each square yard of fabric are examined by means of a light reflectancy spectrophotometer, and only those pieces are retained which have a definite percentage initial light reflectancy with a tolerance of  $\pm 1$  percent. In addition, test samples from each square yard are given a standard washing test, and only those soiled pieces are retained which show a specified increase in light reflectancy as a result of the treatment. The authors have found that results with this test piece are duplicated within narrow limits of error (provided that tests are based on a 50-wash procedure) that the piece is sensitive to slight changes in the washing formula, and that results with the test piece are in accord with practical results in a commercial laundry.

**Factors Involved in Detergency.** A satisfactory detergent must perform a number of functions, of which the following are important: (1) it must wet the fabric or surface to be washed; (2) it must wet the various types of soil which are to be removed from the surface, such as inert soil and oily substances; and (3) it must form a stable emulsion of these soils so as to prevent their re-deposition on the sur-

face from which they have been removed. Fall<sup>39</sup> presented a critical resumé of the conditions suggested by different investigators as entering into detergent action, and employed various ones of these on different types of soap and soap builders.

**Surface and Interfacial Tensions.** The tensiometer of duNoüy<sup>40, 41, 42</sup> has been used by various American investigators to determine the *surface and interfacial tensions* of detergents. In most studies of this type, the instrument is calibrated against analytical weights, and the calibration is tested by determining the surface tensions of water and benzene, using the ring corrections of Harkins and Jordan.<sup>43</sup> Cupples<sup>44</sup> in 1935 published the results of a very thorough investigation on the use of the duNoüy tensiometer to find the wetting and spreading properties of aqueous solutions. Although he was interested primarily in dipping and spraying solutions, he used sodium oleate and oleic acid-sodium hydroxide mixtures in a series of experiments which should be of interest to the scientist who is determining spreading coefficients of detergents.

The *falling drop* method continues to be used as a measure of interfacial tension. One of the most recent American works in which this method is described is that of Snell,<sup>45</sup> in which the interfacial tensions were determined by falling drops of water in oil, and by rising drops of oil in water.

**Adhesion Tension Studies.** Osterhof and Bartell<sup>46</sup> made an attempt to correlate the views expressed by different investigators and writers on the wetting of solids by liquids. They classified wetting into three types—namely, adhesional, spreading, and immersional wetting. They suggested that adhesion tension be adopted as a term to designate degree of wetting, and suggested that apparent differences in conclusions of investigators could be harmonized if the nomenclature in the field were clarified. Bartell and Walton<sup>47</sup> gave various tests for determining the degree of wetting of solids by liquids. They found that data on settling properties for certain powders dispersed through liquids agreed with adhesion tensions as determined by the pressure displacement method. It is possible that the methods developed by Bartell could be applied in determining the wetting of soils and of fibers.

**Miscellaneous Measurements.** The *viscosity* of soap solutions is measured in some laboratories, as an indication of the particle size of the soaps. Viscosity may also play an important part in the stability of the emulsions formed from oily material in the soil and the soap or detergent.

A *sinking time* test for wetting agents was introduced by Draves and Clarkson,<sup>48</sup> in which the time required for a standard skein of cotton to sink in a solution of the reagent was recorded under a specified set of conditions. The effect of variations of temperature, pH, and other conditions on the sinking time were studied by the authors of the test, and the relationship between sinking time and surface tension was

investigated. The relationship between sinking time and concentration of the agent was found to be logarithmic. Although it is not entirely clear what property or properties the method measures, it is apparently a convenient empirical criterion which has become widely used.

Lenher and Smith, on the other hand,<sup>49</sup> pointed out that the Draves sinking time method does not measure the penetration of the fiber by the solution, and proposed an absorption test for determining the efficiency of a penetrating agent.

The *deflocculating power* of soaps is associated with the formation of sorption complexes and suspensions by a combination of soil particles with the detergent. This determines whether or not soil, after removal from a surface, will be kept in a stable suspension, or whether it will flocculate and be redeposited on the surface. McBain, Harborne, and King<sup>50</sup> developed and standardized a method for the rapid, direct measurement of the amount of finely-divided carbon which various soap solutions carry through filter paper. The work of these authors showed that a slight variation in conditions resulted in changes in deflocculating power of the detergent under examination. Chapin<sup>51, 52, 53</sup> proposed and used a graphite test for investigating the fundamental principles of deflocculation in relation to detergency. Fall<sup>39</sup> used manganese dioxide in studies on deflocculation, and others have used umber and rouge.

**Theories Concerning the Action of Detergents.** McBain and his co-workers have published extensively in the field of detergency from 1911 to the present time. McBain and Taylor<sup>54</sup> studied the solubility of detergents in water, their colloidal behavior, and their degree of hydrolysis. McBain and Martin<sup>55</sup> determined the dissociation product and other fundamental properties of alkalies and soaps. McBain<sup>56</sup> drew a number of conclusions from previous work on the constitution and hydrolysis of soap solutions, the composition of soap curd, the osmotic properties and viscosities of soap solutions, and the mechanism of soap behavior toward soil. He further showed the comparative behavior of sodium and potassium soaps at 18° and 90° C., and the influence on properties of the position in the homologous series occupied by the fatty acid radicals in soaps.

McBain and Salmon<sup>57</sup> determined the molecular weights of sodium, potassium, and ammonium soaps, and concluded that the metallic ion was the only crystalloid constituent of a soap, the negative radical being an ionic micelle, made up of normal soap and acid soap. They reported, also, that the addition of electrolytes to soap solutions caused dehydration and a reduction of the proportion of the ionic micelle. Further evidence favoring the theory of the ionic micelle is given by McBain,<sup>58</sup> and by McBain and Bowden.<sup>59</sup> The last two authors reported the results of studies on migration in soap solutions, transport numbers, and ultrafiltration.

McBain<sup>60</sup> reported results on measurements of electromotive force in soap solutions, ultrafiltration, osmotic pressure, and change in freez-

ing and boiling points in solution, which showed that the hydroxyl ion exerts only a very minor influence on the action of soap solutions, and that the activity of soaps can therefore not be attributed to hydrolysis. The results of their tests were believed to confirm further the ionic micelle theory.

McBain <sup>61</sup> used the hydrogen electrode to study the rate of saponification of soaps; McBain and McBain <sup>62</sup> studied the scattering effect of pure sodium oleate sols and gels; McBain, Lazarus, and Pitter <sup>63</sup> determined the effect of temperature upon equilibrium in soap solutions; McBain and Liu <sup>64</sup> determined the rate of diffusion of potassium laurate by means of the Northrop diffusion cell; McBain and Field <sup>65</sup> studied the system potassium laurate-lauric acid over a wide range of temperatures and by several different methods; McBain and Field <sup>66</sup> found two definite crystalline compounds in the system sodium palmitate-palmitic acid—namely,  $\text{Na} \cdot \text{HP}$  and  $2\text{NaP} \cdot \text{HP}$ , and also determined the transition temperatures and the eutectic point; McBain and Stewart <sup>67</sup> similarly investigated the system potassium oleate-oleic acid. McBain <sup>68</sup> determined the diffusion behavior of soaps in relation to osmotic pressures and other properties.

McBain and Watts <sup>69</sup> observed the viscosities of soap solutions and explained the results in terms of two kinds of cohesion within the solution. McBain and McBain <sup>70</sup> developed a formula for the concentration gradient of a neutral molecule or a primary colloid at the isoelectric point. McBain, Kawakami, and Lucas <sup>71</sup> studied the ultrafiltration of potassium laurate solutions with special reference to hydration. They found that, when electrolytes were used as reference substances, a Donnan equilibrium was superimposed upon the filtration effect. They found also that, for high concentrations of ions, the hydration is 12 moles of water for one of potassium laurate.

McBain and Field <sup>72</sup> mapped out phase rule diagrams for three-component systems of potassium laurate-lauric acid-water, and studied the equilibrium conditions of the system. McBain, Bull, and Staddon <sup>73</sup> demonstrated the presence of bound water in the soap curd, and determined the amounts of water present in the hydrates of sodium palmitate and other soaps. McBain <sup>74</sup> included soap in a discussion of the characteristic factors of the colloidal state.

Lawrence <sup>75</sup> presented evidence which seemed to show that the behavior of soap is due to two effects in the molecule: (1) the carboxyl group with its attraction for water, and (2) the hydrocarbon group with its insolubility in water. Lawrence <sup>76</sup> gave further evidence which seemed to show that ordinary soap films do not have a colloidal structure, but consist of a pair of surface layers of adsorbed, molecularly dispersed soap, enclosing between them a true soap solution. He stated that the formation of a stable soap film required (1) the lowering of the surface tension of water to one third its normal value by the formation of an oriented, adsorbed layer of soap, and (2) the formation



of such a layer which has an effective, lateral, cohesive strength greater than the disruptive force of the residual surface tension. In a later paper, Lawrence<sup>77</sup> reviewed the properties of soap micelles.

Johnson<sup>78</sup> considered the mechanism of detergent action from the points of view of wetting, deflocculation, emulsification, and solution, and compared some common detergents on these bases.

Spychalski<sup>79</sup> gave confirmation to the idea of a crystalline micelle by spinning various sodium salts of fatty acids into threads under tension, and examining the threads by means of x-rays. The x-ray diagrams indicated that the micelles have a crystalline structure which is not disrupted even by intensive drying, and that the water in the hydrate filled only the interstices of the fiber. He calculated the space lattice of the micelles, and concluded that the micelles have the form of rectangular prisms with the longest edge parallel to the fiber axis.

Bertsch<sup>80</sup> found that, when sodium oleate is dissolved in water, the ( $-\text{COONa}$ ) groups of the surface layer are oriented toward the interior, while the rest of the hydrocarbon chain is directed toward the exterior.

Bartell and Hershberger<sup>81</sup> studied the degree of wetting of a solid by a liquid, and related this and other properties to the polarity of the solid.

Tate<sup>82</sup> found that detergency in salts of fatty acids is limited to a narrow range of molecular weight of the hydrocarbon chain. If the alkali group constitutes too great or too insignificant a proportion of the molecular weight of the compound, the relation of the water-solubility and -insolubility of the two parts of the molecule is not satisfactory, or in other words, the compound does not possess the desired degree of polarity.

**Soap Builders.** There are four chief types of alkaline builders, or alkaline reagents used to improve the detergency of soaps in water washing. These are carbonates, silicates, phosphates, and caustic soda. To these might be added a less common fifth type—namely, sodium aluminum silicate. The carbonates used are soda ash, sodium bicarbonate, and sodium sesquicarbonate. The silicates include water glass, sodium metasilicate, and sodium sesquisilicate (or orthosilicate), the last of which was recently introduced. It contains 36.9 percent sodium oxide, 23.8 percent silicon dioxide, and 39.3 percent water, as compared with 29.2 percent sodium oxide, 28.3 percent silicon dioxide, and 42.4 percent water in metasilicate. The advantages of sesquisilicate are its increased alkalinity and its ready solubility.

Experimental results on the detergent properties of the alkaline builders differ from one investigation to another, because methods of test are not standardized, and because conclusions have been based on widely different tests without definite knowledge of the significance of each. The comparative detergency efficiencies of various builders have recently been investigated in washing tests by Snell,<sup>83, 84</sup> Rayner,<sup>85</sup> Carter and Stericker,<sup>86</sup> and Morgan.<sup>87, 88</sup> The deflocculating proper-

ties of various alkaline builders have been studied by Carter,<sup>89</sup> Baker,<sup>90</sup> and Snell.<sup>91</sup> Vail<sup>92</sup> discussed the various silicates with relation to their detergency at a meeting of the American Institute of Chemical Engineers, in New Orleans, 1930. Rhodes and Bascom<sup>93</sup> investigated the detergency of alkaline builders quantitatively, both alone and combined with soaps.

**Sodium Hexaphosphate in Hard Water.** The recent introduction of sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub> has placed ordinary soap on a parity with the fatty alcohol sulfates and the Igepons for use in hard water, since this compound ties up calcium and magnesium in complex ions and prevents them from forming insoluble calcium and magnesium soaps. Gilmore<sup>94</sup> described the method of making sodium hexametaphosphate (known in the textile industry as "Calgon") by heating monosodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) to form ( $\text{Na}_2\text{P}_2\text{O}_7$ ). Further heating at a low temperature converts the latter to sodium metaphosphate ( $\text{NaPO}_3$ ). Upon heating this to redness, it polymerizes into the hexametaphosphate. The *pH* value of this compound is about 5.5 in dilute solution. The present trend in the use of this reagent is as an adjuvant in every type of cleaning which is conducted in hard water. The applications of sodium hexametaphosphate as an assistant in the textile industry is described by Bell.<sup>95</sup>

**Enzymes as Detergents.** Enzymes have had some use in general laundry procedure in Germany<sup>96</sup> for a number of years. In the old detachable collar days in this country, amylolytic enzymes were employed in some laundries to remove starch and simplify laundering. At present, however, the use of enzymes in laundering and drycleaning is restricted to the employment of proteolytic enzymes for the removal of blood and other albuminous stains in hand stain removal processes.

Keeney and Mack<sup>97</sup> conducted laboratory and practical tests in which standard soiled fabrics coated with starch and with albuminous stains were treated with amylolytic and proteolytic enzymes, alone and together, in one of the baths of a recommended laundry procedure. Amylolytic enzymes were found to improve detergency efficiencies in the case of starched fabrics, and proteolytic enzymes assisted in removing soil by digesting albuminous stains, provided that conditions of concentration, *pH*, and temperature were suitable for the enzyme in question.

Powers<sup>98</sup> gave the optimal conditions for the action of certain enzymes, and discussed methods of measuring enzyme activity.

Nopitsch<sup>99</sup> investigated the effect of enzymes on the strength of cotton fabrics and concluded that there was no evidence of cellulose destruction throughout his work. Keeney and Mack<sup>97</sup> extended his investigations to include a larger number of enzymes under a wide variety of conditions of time, temperature, *pH*, and concentration, and found no case in which the loss in breaking strength of a cotton fabric was greater when enzymes were present than when they were absent, all other conditions of the test being similar.

**Bleaching Agents.** Bleaching agents, principally sodium hypochlorite and similar reagents, have long been used in American laundry practice. Contrary to the popular belief, they are of no value in general soil removal, although they are effective in the removal of various stains, and to some extent in the maintenance of the whiteness of white fabrics. The destructive action which sodium hypochlorite exerts on textile fibers has eliminated its use with protein fibers, and has made its application to the cellulose fibers one which calls for extreme care.

The shortcoming of the chlorine bleaches just mentioned has opened up two important lines of research in this field: (1) investigations of the ideal conditions for using the chlorine bleaches; and (2) searches for chlorine bleach substitutes.

A study of the strength losses in cotton fabrics under a wide variety of conditions was made at the Massachusetts Institute of Technology.<sup>100</sup> The influence of chlorine bleaches on the whiteness and breaking strength of fabrics was studied at the American Institute of Laundering.<sup>101</sup> Oesterling and Mack<sup>38</sup> have found that the  $pH$  of a bleach bath has a great influence on the degree of degradation of cellulose, the breakdown being very small at high  $pH$  values, and very great when the  $pH$  is low. They found that chlorine bleach baths made in a large variety of ways, either from sodium or calcium salts, were similar in their effect on the breaking strength of fabric, if the chlorine concentration, the  $pH$ , and other conditions were the same. They found further that moderately low temperatures (110 to 140° F.) and low concentrations of chlorine were as effective (in stain removal and whiteness retention), as higher temperatures, while causing only small losses in fabric strength. They also found that increase in breaking strength losses of a fabric showed a numerical relationship to copper number of the fabric, which indicates that the loss in strength is due in considerable measure to chemical breakdown within the fiber.

Among the substitutes for chlorine bleaches which have been proposed, or actually introduced into practice in this country, are sodium hydrosulfate, hydrogen peroxide, and various borates. Keeney and Mack<sup>97</sup> found that sodium hydrosulfate produced insignificant losses in the strength of cotton under a considerable variety of conditions, but was unsatisfactory as a laundry bleaching agent because of its yellowing effect upon fabrics. Oesterling, Mack, Krawiec, and Ebert, in unpublished work done at The Pennsylvania State College, have investigated hydrogen peroxide as a laundry bleach through a wide range of conditions, and have found that it is more effective in stain removal and whiteness retention than chlorine bleaches of similar concentration, and that it causes a smaller degree of breakdown in cotton than is caused by the other type of bleach. It may also be used, with proper precautions, on wool and silk fabrics, and on certain dyes. Its use requires care, however, and there is a definite concentration, temperature,  $pH$ , and time range within which it is most satisfactory. Various

borates and perborates have been investigated as bleaching agents abroad,<sup>102</sup> which have a limited application in laundry and drycleaning practice in this country. Bleaches of the borate and perborate type are being studied at present in various American laboratories to determine their possible utility for large-scale laundry use.

**Discussion.** A survey of the literature in the field of detergents and detergency shows that a vast amount of valuable data has been accumulated by American investigators working in this field during the past few years. It is frequently difficult to relate the data of one investigator with that of another, however, because of the following facts: (1) there is no uniformly accepted standard procedure for the practical measurement of detergency; (2) methods of making chemical and physical tests on detergents have not been standardized; and (3) there is no agreement among investigators as to the significance of chemical and physical tests after they have been made. Too frequently, an investigator assumes that one or two measurements give all of the information necessary about a certain detergent. The factors involved are not simple, however, and several types of chemical and physical tests must be made and interpreted in order to explain the behavior of a detergent in practical tests.

The chemical and physical tests on detergents which have been emphasized in the literature include the following: surface, interfacial, and adhesion tension; emulsion number and foam number, or height of suds; deflocculation; penetration, sinking time of fibrous material in a solution of the detergent; lubrication, and absorption; viscosity of solutions of the detergent; solubility and solubilizing effect of the detergent;  $pH$ ; and chemical stability.

Surface tension has been used by some investigators as a measure of the activity of the detergent. Actually, a low surface tension is merely indicative of strong surface or capillary active substances, and does not necessarily denote that the substance has other properties required in a detergent. Adhesion tension seems to be directly related to surface tension, while interfacial tension depends upon the polarity as well as the type of groups in the molecule of the detergent. The emulsification of oil by a detergent depends upon a low interfacial tension, while the foam number depends upon the surface tension, the type of micelle, and other factors. The balance between the surface tension of oil, the surface of the solution of the detergent, and the interfacial tension between the two determines the spreading coefficient, and shows whether one liquid will spread over or wet another.

Good detergents apparently have the property of dispersing and suspending particles of soil, and they form films of sufficient viscosity to produce stable emulsions. The viscosity of a solution of a detergent also features in the ease of preparation and convenience of handling soap solutions. Lubrication, penetration, and absorption of detergents appear to play a part in the displacement of soil in fibers, and the production of a clean fabric with certain desirable properties

as to finish. At the same time, absorption is important in its relation to the rate at which the detergent is removed from the bath. Such factors as pH and chemical stability are important also.

The evaluation of the properties just discussed, either singly or in combination, must depend upon parallel washing tests in which soil removal from fabrics and whiteness retention are determined.

The author wishes to thank Lawrence P. Hall for invaluable assistance in the writing of this chapter, and Mary D. Caulk for helpful assistance with the bibliography.

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# Chapter XXI.

## Cellulose and Paper.

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The very considerable increase in interest and research activity in the fields of cellulose and paper, noted by this reviewer in the introduction to Chapter VIII of the 1933 Annual Survey, has continued throughout the past two years. Technical papers and patents have so increased in number that only the barest discussion is possible of the various literature references cited, while the patent literature must of necessity be entirely omitted. A recent TAPPI publication<sup>1</sup> contains 71 pages of U. S. patents granted in 1934 in the fields of cellulose and paper and lists only the titles, names of patentee, and necessary dates and description. The year 1935 has been even more prolific.

Two historical surveys should be included in this review. The first, by Johnson,<sup>2</sup> refers to the development of the pulp and paper industry in the United States. The second, that of Esselen,<sup>3</sup> deals with the rayon industry. A compilation of current researches on pulp and paper making in nineteen laboratories has been prepared by West.<sup>4</sup> Shaw<sup>5</sup> summarizes the research work being carried out with the experimental paper machine at the Bureau of Standards.

The scope of technical control in pulp and paper manufacture is indicated by Kidder,<sup>6</sup> Phelps,<sup>7</sup> and Minor.<sup>8</sup> Heritage<sup>9</sup> discusses the fundamental relationship between research and operation from the standpoint of the product manufactured, and management, research, and operation.

A new laboratory has been established at the University of Michigan with facilities for pulp and paper testing. Additional laboratory and semi-plant construction is in process at The Institute of Paper Chemistry, whereby laboratory facilities will be about doubled.

Reference should be made to the symposium on the nature of cellulose held under the auspices of the Cellulose Division of the American Chemical Society at the spring meeting in New York in 1935. Review papers were prepared by authorities in the various fields to cover the chemical and physical properties of cellulose, x-ray structure and molecular weight determinations, the micro-structure of cellulose fibers, and the formation of cellulose in membranes.

**Wood.** The source of the future pulpwood supplies in the United States is a matter of general interest. Curran<sup>10</sup> has made a survey of the situation and discusses the possible use of Engelmann spruce, ponderosa pine, redwood, and the western cedars in the remote areas of the country. Munger<sup>11</sup> and Davis<sup>12</sup> describe the wood stands of the Pacific Northwest. The latter refers particularly to standing hemlock, spruce, noble fir, and three species of the white fir. The above reference by Curran shows the trend away from spruce, which in 1899 furnished 76 percent of the pulp and in 1932 but 37 percent, toward hemlock, southern yellow pine, balsam fir, and jack pine.

Improvement in yield and quality of pulp wood by controlled hybridization of forest trees in the poplar breeding project of the Oxford Paper Company is described by Schreiner.<sup>13</sup> These new hybrid poplars are decidedly better than the native poplars for they grow more rapidly, are more easily propagated and are more resistant to disease. Many will produce wood with a longer average fiber length and somewhat higher density than the native poplar used in Maine for the preparation of soda pulp.

The work of the Forest Products Laboratory in the evaluation of additional pulp woods has been continued so as to include the short leaf pine (*Pinus echinata*), cajeput, white mangrove, Australian pine, and Cunningham pine. Bray and Paul<sup>14</sup> report that chemical analyses of the pulp obtained from the first wood showed no outstanding evidence adverse to the production of good quality pulps of average yields by the kraft process. Curran, Schwartz, and Bray,<sup>15</sup> in discussing the kraft cooking of Florida-grown species of the last four, point out that the pulps are short fibered and inferior to pulps from the common pulpwood species.

Stamm<sup>16</sup> has continued his investigations of the colloidal characteristics of wood. Measurements have been made of the equilibrium permeabilities of softwoods to air at different relative vapor pressure. On the basis of these, a new means has been developed for determining the distributions of size of openings in a porous membrane. He and Seborg<sup>17</sup> have measured the adsorption compression of water on Sitka spruce and white spruce heartwood sawdust, cotton linters, alpha cellulose, a normal sulfite pulp, and the same pulp in a "highly hydrated" condition in benzene. The evidence indicates that this force is of the order of several thousand atmospheres. A means of minimizing wood shrinkage and swelling in wood, involving the impregnation of green or dry wood with a water insoluble oil or molten wax or resin has been based by Stamm and Hansen<sup>18</sup> upon the primary replacement of water in the wood with Cellosolve and the subsequent replacement of the Cellosolve by waxes or resins at temperatures above their melting point. The process serves as a combined seasoning and anti-shrink impregnation treatment for refractory species.

Stamm<sup>19, 20</sup> has likewise measured the effect of inorganic salts on the swelling and shrinking of wood, as well as other factors affecting

dimension changes such as result from variations in moisture content. Stamm and Loughborough<sup>21</sup> have applied thermodynamic methods to the calculation of equilibrium moisture content, relative pressure curves and isotherms, fiber saturation points, temperature curves, differential heats and free energy changes of swelling, isosteres, and entropy changes with swelling for Sitka spruce.

Buckman, Schmitz, and Gortner<sup>22</sup> have studied certain factors influencing the movement of liquids in wood. These include: (a) the relative effectiveness of the maximum and average pore diameter of the openings in the pit membranes for woods at different moisture contents, (b) the influence of pressure on the rate of flow of water through wood, and (c) the movement of organic liquids and salt solutions through wood. The diffusion of neutral molecules such as urea, glycerol, and lactose from aqueous solutions with samples of wood of known capillary dimensions has been investigated by Cady and Williams.<sup>23</sup> Measurements have been made with heart and sapwood in transverse radial and semi-tangential sections.

The series of articles on the chemistry of woods has been continued from the laboratory of the New York State College of Forestry. Peterson, Maughan, and Wise<sup>24</sup> have investigated the water-soluble polysaccharide from the European larch (*Larx decidua* Null) and establish its identity with the carbohydrates from the two American species; namely, an arabogalacton containing 11.63 percent anhydro-arabinose and 81.95 percent anhydrogalacton. Its separation as an ash-free chemically homogeneous material was effected by electrodialysis.

Herty and Rasch<sup>25</sup> have prepared rayon from southern pine pulp and have found that with the exception of the higher ash content, it compares favorably with rayon made from commercial rayon pulps. Brannock, Bunger, and Doud<sup>26</sup> check these observations in the main.

**Cellulose.** A large number of significant articles relating to the physical characteristics of cellulose and cellulose fibers have appeared. Stoops<sup>27</sup> has measured the dielectric constant and power factor data on dried glycerol-free Cellophane for a wide range of temperature and frequency. The dielectric constant for Cellophane is found to be nearly twice that of cellulose acetate. An explanation of this based on a variation in chemical structure is advanced. Sanders and Cameron<sup>28</sup> find the x-ray unit cell of the cellulose in cotton stalks and cusp to be the same as that in linters, and spruce, pine, and poplar wood. They trace differences in the physical properties of products from cellulose of different origins to the micellae in the fibroid structure.

The sorption of water by cellulose as an index of the fine structure of the gel has been considered by Sheppard and Newsome.<sup>29</sup> Alpha-pulp has higher sorption than cotton cellulose, approaching mercerized cellulose. Sorption is unaffected by heating (hydration), which effect depends upon an increase in external surface or dispersity. Bancroft and Calkin<sup>30</sup> believe that the reaction of caustic soda and cellulose is entirely described by adsorption rather than by compound formation.

The adsorption of organic liquids by cellulose products has been investigated by Wiertelak and Garbaczówna,<sup>31</sup> who have been interested in the extent to which the adsorption of organic liquids will interfere with the standard analysis of wood and cellulose products. They find ready adsorption of alcohols, pyridine, and benzene-alcohol mixtures, which liquids are not removed from the fiber by heating at 105° C. Neither benzene nor gasoline is adsorbed.

The sorption of dyes by cellulose has been considered by Clark and Southard<sup>32</sup> and by Friedman and Kuykendall.<sup>33</sup> Such work throws light both on the mechanism of commercial dyeing and also on the fine structure of fibers. The latter paper describes particularly the effect of pH variations on the absorption. Lenher and Smith<sup>34</sup> show that electrolyte-free substantive dyes in water solutions are only slightly absorbed by cotton of low ash content, that the addition of an electrolyte induces adsorption, and that a maximum particle size exists above which dyes are not readily adsorbed by cotton. The particle size and the salt sensitivity of the dyes are the controlling factors in their dyeing characteristics.

Rowland<sup>35</sup> presents a critical survey of recent work on selected topics concerning the colloidal behavior of cellulose as related to the technical problems of paper making.

Two papers of interest bearing on the formation of carbohydrates or cellulose membranes are those of Sponsler<sup>36</sup> and Farr.<sup>37</sup> Sponsler has followed under the microscope the rate at which cell wall material is developed as a new cross wall is formed in the growth of green algae. The material is of carbohydrate origin. Farr traces the cell membrane formation in young cotton fibers to the existence of cellulosic elliptical particles covered with thin layers of pectic materials. These may be freed from the pectins by treatment with hydrochloric acid (sp. gr. 1.19). They can neither be regarded as micellae nor as macromolecules. Three other papers concerning the work of Farr and Eckerson<sup>38, 39</sup> and Farr and Sisson<sup>40</sup> give additional material on this subject.

Important studies on the molecular weights of cellulose and cellulose derivatives have been reported by Kraemer and Lansing.<sup>41</sup> Comparisons are presented for molecular weight determinations by osmotic pressure and viscosity measurements, end group determinations, and ultracentrifugal analysis. The authors describe the latter method as being the most reliable. The influence of solvation on molecular association and molecular weight values for cellulose are discussed. These range between 60,000 and 180,000.

Kurth and Ritter<sup>42</sup> have removed the easily hydrolyzable fraction from the holocellulose of spruce and maple wood by treatment with one percent sulfuric acid. This gives a fraction which, under the older methods of analyses, has always been mixed with other wood constituents. It is composed of constituents containing methoxyl, carboxyl, acetyl, and formyl groups and hydrolyzing to mannose, glucose, galactose, arabinose, and xylose. Salley<sup>43</sup> has studied the effect of ferric

salts and alkali in carrying on an oxidation of mannitol in aqueous solution. The factors increasing the rate of auto-oxidation are concentration, temperature, and light. In the latter case, the increase in rate is directly proportional to the light absorbed. Oxidation inhibitors have no effect on this system. A comparison is drawn to the well-known behavior of cellulose.

The utilization of bagasse as a source of cellulose has been considered. Lathrop and Munroe<sup>44</sup> show how the sugar cane may be preserved during storage by piling the bales in such a manner that the heat of carbohydrate fermentation is used to raise the temperature of the interior bales to a pasteurizing temperature. Payne<sup>45</sup> pulps bagasse by digesting with two percent nitric acid at 90-100° C. for one hour, followed by two alkaline treatments. The method is said to be applicable to large scale production.

A quantitative method for the separation of cellulose acetate, silk, regenerated cellulose rayons, cotton, and wool has been developed by Mease and Jessup.<sup>46</sup> After desizing the acetate silk is removed with acetone, and silk and regenerated cellulose rayon are removed with calcium thiocyanate solution of 1.20 and 1.36 sp. gr., respectively. Cotton and wool are determined by the solution of cotton in aluminum chloride with heat or the solution of the wool in the potassium hydroxide solution. The method is accurate for each fiber present to within two percent of the weight of the specimen analyzed.

The physical properties of a series of the cellulose triesters of homologous fatty acids from the acetates to the stearates, as measured by Sheppard and Newsome,<sup>47</sup> show that the cellulose character is progressively submerged as the length of the side chain is increased. The structure of the solids is interpreted from x-ray data and by spreading and wetting experiments. Kirkpatrick<sup>48</sup> has made a fire-resistant cellulose acetate sheet by incorporating 20 percent or more of triphenyl phosphate or a mixture of triphenyl phosphate and methyl phthalyl ethyl glycollate. The latter improves flexibility at the expense of fire resistance. Noncombustible fillers may also be incorporated in the latter. White<sup>49</sup> describes how to avoid difficulties in the production and application of cellulose acetates for the various uses.

A double dyeing method for estimating the increase in specific surface of beaten nitrocellulose has been devised by Phillips,<sup>50</sup> and has been confirmed by microscopic analysis. This permits a differentiation impossible by the settling test. Gloor<sup>51</sup> lists the properties of low viscosity nitrocellulose of varied nitrogen content. He states that the film properties of these low viscosity types result from the degradation of cellulose residues and vary with the nitrogen content, viscosity, formulation, and plasticizer. McBain, Grant, and Smith<sup>52</sup> have measured the viscosity of nitrocellulose in over 100 solvents and solvent mixtures. They emphasize that the chief factor in the apparent viscosity of nitrocotton solutions is structural viscosity due to colloidal aggregates of easily varied degree of ramification and dismemberment. Time

experiments at 55° C. extended to three years have yielded solutions approaching the viscosity of the pure solvent within a few percent—an enormous drop in viscosity. In some cases these low viscosities may again increase and even set to a jell. Four new methods for determining degree of solvent power are briefly indicated.

**Lignin.** Phillips<sup>53</sup> has presented a 51 page survey of the chemistry of lignin with 304 literature references. Phillips and Goss<sup>54</sup> have investigated the lignin isolated from barley straw. Two fractions are found, one with the formula  $C_{40}H_{48}O_{15}$ ; the other,  $C_{40}H_{42}O_{16}$ . The chemical characteristics of maple and spruce lignin, isolated by various methods, are described by Harris, Sherrard, and Mitchell.<sup>55</sup> Cold sulfuric acid lignin is free of carbohydrates and contains all the methoxyl not accounted for in the carbohydrates of the wood. Hydrochloric acid lignin has lost methoxyl and contains carbohydrates. Cuprammonium lignin also contains carbohydrates. The number of hydroxyl and unsaturated groups from hard and soft wood lignin is different. Results from chlorination and methylation show that lignin is little changed during isolation by the sulfuric acid method. There is some evidence that lignin in wood is combined with carbohydrates. The reason for the difficulty in the use of Douglas fir for sulfite pulp has been ascribed by Bailey<sup>56</sup> as being due to a difference in the structure of the lignins. Bailey believes that Douglas fir lignin consists of four rather than three polymerized coniferyl aldehyde residues in terms of the Klason lignin structure, and because of this the wood is more difficult to delignify than spruce. Ammonia lignin has been oxidized by alkaline halogen solutions. Alkaline iodine oxidation proceeds quantitatively and forms a compound containing carboxyl groups and iodine<sup>56a</sup>; iodoform is also isolated as one of the products of reaction. Alkaline bromine solutions yield carbon tetrabromide. The authors postulate the presence of a secondary group of the type  $CH_3CH-(OH)$  in the lignin molecule.

A number of papers relating to the microbiological decomposition of lignin have appeared. Levine, Nelson, Anderson, and Jacobs<sup>57</sup> attempted without success to develop a specific lignin-digesting anaerobic flora. Alkaline lignin when added to an actively digesting sludge produces no gas, and, when used in conjunction with fermenting corn stalk flour or packing house sludge, inhibits the gasification of the latter materials. This is not due to toxic action of the lignin on the bacterial flora, but to chemical combination with the production of complexes resistant to microbial decomposition. Boruff and Buswell<sup>58</sup> have investigated the anaerobic fermentation of lignin in cornstalks and the lignin isolated by four methods, and show that appreciable quantities ferment to carbon dioxide and methane in the natural state, while isolated lignin ferments very slowly and incompletely. Waksman and Smith<sup>59</sup> deal with the problem of the transformation of the methoxyl groups of lignin in the decomposition of plant residues. The relation of this to humus formation in soils, peats, and composts is discussed.

Mitchell and Ritter<sup>60</sup> have analyzed three fossil woods mined from

the Miocene auriferous gravels of California, and find that a marked decrease has occurred in the extraneous and carbohydrate content of the wood, while the lignin contents are abnormally high. On the basis of the original wood, the lignin has decreased less than any other constituents. Decomposition of the cellulose appears to be due to hydrolysis rather than fungus attacks.

**Groundwood.** Curran, Schafer, and Pew<sup>61</sup> find that much of the color in western hemlock groundwood is due to reddish inclusions present in the ray cells. These inclusions resemble chemically the material extracted by alkali from the bark and are therefore probably tannin or tannin derivatives. The fine-fibered portion contains more coloring matter than the coarse-fibered portion. Bisulfite and hydro-sulfite improve this color, while certain oxidizing agents in alkaline solution, especially hydrogen peroxide, are effective bleaching agents but of doubtful economic value. Lowen and Benson<sup>62</sup> have prepared plastics from groundwood pulp, utilizing the pentosans for the production of a resinous adhesive to serve as a binder in place of extraneous adhesives. The products are of excellent appearance and are suitable for various purposes. They are slightly brittle and not very resistant to boiling water.

**Cooking Process.** Aronovsky and Gortner have continued their series of articles on the cooking process. In Part V<sup>63</sup> they describe the use of sodium sulfite and aspen sawdust, in Part VI<sup>64</sup> sodium sulfide, and in Part VII<sup>65</sup> sodium hydroxide and trisodium phosphate. They consider all these chemicals to be strong pulping agents.

In Part VIII<sup>66</sup> they tell of the formation of volatile acids when aspen sawdust is cooked with sodium carbonate for two hours at 170° C. The production of volatile acids is attributed to saponification. Aronovsky<sup>67</sup> has summarized these previous reports, especially from the standpoint of the main components of the residual woods and liquors.

A continuous pulp cooking system has been described by Braun and Lundberg.<sup>68</sup> The object has been the development of a continuous cooking, washing, and bleaching system with separate units for each step. No plants have yet utilized the process.

**Sulfite Process.** A number of papers have appeared which describe work on some phase of the sulfite process. The commercial installation and operation of a new spray type sulfur burner is referred to by Kress, Swanson, Porter, and Smith.<sup>69</sup> The formation and dissociation of sulfur trioxide in sulfur burner gases from the above spray burner has been measured by Browning and Kress.<sup>70</sup> The variables covered include temperature, the composition of the gas, and catalytic effects of various materials of construction. Frank and Beuschlein<sup>71</sup> have investigated the equilibrium relations in the system calcium oxide-sulfur dioxide-water under conditions similar to the raw acid coming from the absorption towers. Beuschlein and Conrad<sup>72</sup> have applied the film concept to the operation of sulfite acid towers and describe the role played by the several fluid films which control

the rate of sulfur dioxide absorption. Pressure-composition curves are presented for the system described above.

McGovern and Chidester <sup>73</sup> present data to show the effect of chip length upon the time of penetration and pulping of western hemlock heartwood, the chips ranging from  $\frac{1}{8}$  inch to  $1\frac{1}{8}$  inches. Time of penetration increased in a parabolic manner with increasing chip length. The optimum strength values were reached in pulps from chips  $\frac{1}{4}$  to  $\frac{1}{2}$  inch long, but no significant variation in rate of pulping was noted. Hrubesky and Chidester <sup>74</sup> have measured the rate of penetration of calcium bisulfite liquor in western hemlock chips and the time required to burn the chips under varying conditions. Benson, Erwin, Hendrickson, and Tershin <sup>75</sup> pulped Douglas fir by an ammonia base liquor with and without a pre-treatment with 5 percent ammonia at temperatures below 70° C. Young Douglas fir and pre-treated Douglas fir approach spruce and hemlock. Old Douglas fir pulps are distinctly lower in quality.

Sulfite waste liquor studies have appeared in a considerable number. Warrick and Holderby <sup>76</sup> describe recent waste liquor developments, emphasizing especially the Howard and Paulson processes. Howard <sup>77</sup> also has written of his process, in which the waste liquor is fractionally precipitated with lime, whereby three-fourths of the pollution loading is removed, while Wells <sup>78</sup> has described the Paulson process. Phillips, Goss, Brown, and Reid <sup>79</sup> treat the dry residue of sulfite waste liquor with ammonia at high temperatures and have investigated the fertilizer value of this ammoniated material containing up to 10.5 percent N. It has some value but is not the equal of either dried blood or a mixture of sodium nitrate and ammonium sulfate as a source for mixed fertilizer. O'Dell and Greenlaw <sup>80</sup> show that under properly controlled conditions, ponding and aeration will greatly reduce the biochemical oxygen demand of waste sulfite liquor, thus eliminating part of its polluttional effect. Pollock and Partansky <sup>81</sup> describe a simple and inexpensive method for the determination of sulfur in sulfite waste liquor and other organic compounds. Leitz, Sivertz, and Kobe <sup>82</sup> have measured the *pH* of sulfite waste liquor with the glass electrode and find a *pH* of 9.6 to be optimum for the precipitation of organic material with ammonia. Winiecki <sup>83</sup> describes the use of "Raylek B" as a road binder and dust palliative. "Raylek B" is produced by concentrating waste liquor. The process leaves the material with an acidity about a fourth as much as vinegar. The material has been satisfactory as a patching material and is now under test as a binder for permanent road construction. Kobe and Centenero <sup>84</sup> show that the amount of combustible sulfur in sulfite waste liquor is much below the total sulfur content. Methods for removing sulfur dioxide from the stack gas are also discussed.

Billington, Chidester, and Curran <sup>85</sup> have outlined a method for the conversion of sodium sulfide in the ash obtained from burning waste



soda-base sulfite liquor to sodium carbonate which is re-used in the preparation of fresh cooking liquor.

**Alkaline Pulping.** An investigation by Holzer<sup>86</sup> of the coloring matter in pine kraft pulps reveals that this material appears to be related to the phlobotannins. Analysis shows organic sulfur and further evidence leads to the conclusion that the material is probably a sulfur derivative of the phlobotannins. Organic sulfur content in kraft pulp is dependent upon the sulfidity of the cooking liquor; in bleached and unbleached pulps the color varies with the sulfur content. Kress and McIntyre<sup>87</sup> have followed the distribution of sulfur during the kraft cooking process. In carrying out the work, it was necessary for them first to evaluate the methods used in the estimation of sulfide. Kress and Harrison<sup>88</sup> find that pulps made from kraft cooks using improperly settled white liquor have poor strength and color, due possibly to the presence of mechanically entrained calcium carbonate.

Pillow and Bray<sup>89</sup> have pulped compression wood by the kraft process and find, in contrast to normal wood, a lower yield of crude pulp with poorer physical and chemical characteristics and an increase in bleach requirements. Gordon and Creitz<sup>90</sup> remove the mercaptans and alkyl sulfides from the non-condensable gases present in the kraft relief gases by spraying a solution of hypochlorite into the gases. The aqueous layer of the condensate as well as the condensate from the evaporation of the black liquor are similarly treated. The odor is not entirely removed and the author states it to be unpractical to destroy all the mercaptans by the alkaline treatment.

**Pulp Properties.** Lary and Davis<sup>91</sup> have determined the effect of a variation in  $pH$  between 4 and 9 upon the freeness of chemical and groundwood pulps. With the chemical pulps, the drainage time increases as the  $pH$  is increased from  $pH$  4 to a maximum in the range  $pH$  5-6; it then decreases to reach a minimum at  $pH$  9. The effects are of considerable magnitude in the case of samples given the most refining. With groundwood the effect is quite different; above  $pH$  6 the values are erratic, below this the drainage time increases 60 per cent in going from  $pH$  4 to  $pH$  4.4.

McGregor<sup>92</sup> has studied the relation between the physical characteristics of pulp and their chemical components, using two rag pulps, an alpha pulp, and a Mitscherlich sulfite. These he degraded by various means to definite viscosities and then ran strength tests and chemical analyses. There appears to be a definite relation between viscosity and fold quality within the various types of pulp. In general the relation between the properties of the pulps and the degrading influence depends upon the type of degradation.

**Beating and Hydration.** Lewis and Gilbertson<sup>93</sup> find that the temperature effect in the beating of rag stock is a matter of some importance on the strength of hand sheets prepared from the stock. The physical characteristics such as fold, tear, tensile, and Mullen are much lower for stocks beaten hot than for stocks beaten at lower tem-

peratures, while the chemical constants bear no relation either to time or temperature of beating. The effect of beating on fiber structure is described by Weil,<sup>94</sup> who indicated the purpose of beating as two fold, first to bruise the various membranes and damage them in such a way that the first and subsequent layers of fibrils are loosened without harming the length of the fiber, and second, to form a fiber debris and structureless slime or gel which serves to cement the fibers in the dried sheet of paper.

**Bleaching.** Henderson<sup>95</sup> describes the art of bleaching in theory and in practice, dealing particularly with the basic chemistry of the reaction between chlorine and lignin. Recent developments in the bleaching of chemical wood pulps are surveyed by Rue.<sup>96</sup> A method for the determination of available chlorine in hypochlorite solutions by direct titration with sodium thiosulfate is outlined by Willson.<sup>97</sup>

**Sizing.** Little work of fundamental interest in sizing has appeared in the literature of the United States during the past two years. Dreshfield<sup>98</sup> has discussed the agents and methods which may be used to make paper repellant to different liquids. Various rosin sizing methods in commercial use have been described, Montgomery and Batchelor<sup>99</sup> taking up the Delthirna process; Kennedy,<sup>100</sup> the Bewoid, and Sinclair<sup>101</sup> and Neitzke,<sup>102</sup> the Bennett size making process. Descriptive papers have been published by DeCew<sup>103</sup> and Stevens.<sup>104</sup> Sutermeister<sup>105</sup> has completed a very excellent review of the literature of sizing, going back to 1900 and referring to the more important works prior to that date. Krimmel<sup>106</sup> points out the losses in the manufacture of rosin size milk with a number of hot processes and gives a practical method for measuring these losses.

**Permanence.** Work has been continued in the laboratories of the Bureau of Standards and of the Brown Company on problems relating to the permanence of papers. Richter<sup>107</sup> describes experimental work carried on in which papers have been exposed to natural sunlight for periods of time. He finds that losses in tear, tensile strength, and Mullen are minor as compared with the loss in fold. He suggests special sizing agents for use in papers so as to enable them to withstand the action of sunlight more successfully. While the folding strength of a paper is enhanced by tub sizing with glue, this increment in fold is largely lost when the papers are exposed to sunlight. He has likewise exposed papers for an extended period in a circulating air current maintained at 38° C. He reports that the physical changes correlate well with the corresponding changes taking place with the same types of paper subjected to the 100°, 72 hour test. He notes that severe chemical oxidation of an unbeaten cellulose fiber is reflected in a marked sacrifice in the stability of the paper produced.

Rasch and Scribner<sup>108</sup> report on a series of 33 papers tested for chemical purity and strength after four years of normal aging. The folding endurance during this time has undergone marked change. The papers are placed in about the same order of stability by normal

aging as by the accelerated aging test. Scribner<sup>109</sup> further reports on an investigation relating to the preservation of old newspapers. For retarding decay he recommends the use of Japanese tissue paper or transparent cellulose acetate sheeting. Weber, Shaw, and Back<sup>110</sup> find that the ordinary fumigants, such as hydrocyanic acid gas, carbon bisulfide, etc., have no significant deleterious effect on the life of the paper and conclude that these can be used safely for killing insect life in records of permanent value.

Zimmerman, Weber, and Kimberly<sup>111</sup> report that the life of written records depends upon the stability of the ink as well as upon the paper. Iron gallotannate prepared according to the government formula for standard writing ink greatly accelerates the deterioration of papers in the heat test. They recommend an ink made with ammonium-ammonium oxyferrigallate.

Shaw, Bicking, and O'Leary<sup>112</sup> have carried on a study of the relation of some of the properties of cotton rags to the strength and stability of experimental papers made from those rags. The results demonstrate that stable paper can be made from new rags and confirm the belief that high acidity from excess use of alum in rosin sizing has a marked deteriorating effect upon paper. They recommend a pH of 5.0. Blaisdell and Minor<sup>113</sup> have done some work on the permanence of poor grades of paper, such as those made from cheap wood pulps. Of special interest is their conclusion that a marked change of copper number with oven or light aging may be considered as indicative of a definite loss of absorbency with natural aging.

Of significance is the description by Farquhar<sup>114</sup> of the special edition of 25 copies of scientific works being printed by the University of California Press on a permanent 100 percent rag paper. These copies are being distributed to a selected list of repositories throughout the world.

**Paper.** High opacity papers continue to receive attention. Belcher,<sup>115</sup> Cyr,<sup>116</sup> and Steele<sup>117</sup> discuss the advantages resultant from the use of zinc pigments. Smith<sup>118</sup> brings out the fact that the zinc pigments slow up the rate of growth of organisms causing slime and discoloration. Willets<sup>119-122</sup> reports on the use of titanium oxide as a pigment and in the last reference takes up in a comprehensive manner the factors favoring retention in the sheet. Sutermeister<sup>123</sup> concludes that the formula for satin white is probably  $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{CaSO}_4 \cdot 31 \text{H}_2\text{O}$ .

The use of rubber latex in paper is reviewed by Townsend<sup>124</sup> and by Birchard.<sup>125</sup> A method for the de-inking of paper involving the use of sodium silicate and fatty acids is outlined by Snyder and MacLaren.<sup>126</sup> For the removal of color from broke, Binns<sup>127</sup> recommends the use of zinc hydrosulfite and outlines the conditions for its use. As a softener and plasticizer in paper, Leete<sup>128</sup> has used sugar combinations. The application of nitro-cellulose emulsions to paper is described by Hollabaugh.<sup>129</sup> Rancidity-retarding wrappers may be prepared by

incorporating colored materials which absorb blue and ultra-violet light, according to Morgan.<sup>130</sup>

Piper<sup>131</sup> describes a method for removal of oil from oil-impregnated papers for testing purposes.

Bailey<sup>132</sup> presents a number of photomicrographs of thin paper sections; these demonstrate the characteristics of the fiber to fiber bond. The significant sheet properties for use in developing paper specifications are listed by Baird.<sup>133</sup> The basic principles of sheet formation as they relate to the head box and slice have been considered by Bearce,<sup>134</sup> while Rubin<sup>135</sup> takes up the factors governing sheet formation on the Fourdrinier wire. Doughty<sup>136</sup> outlines the effect of mechanical treatment of fibers on sheet structure. Fundamental information on the drying of paper is presented by McCready<sup>137, 138</sup> and by Adams.<sup>139</sup>

Anderson<sup>140</sup> discusses the possibility of manufacturing newsprint from southern pine under commercial operating conditions. The southern fibers apparently do not felt as well as the northern spruce fibers nor are their surface characteristics as good. Lee<sup>141</sup> reviews the work of Herty and his associates on the pulping of southern pine.

Stamm<sup>142</sup> and Baker<sup>143</sup> consider the advantages to be gained by the use of white water in various mills and on various types of machines under differing conditions. Chase<sup>145</sup> states that the acidity in paper may be measured by determining the H-ion concentration of the tray water and outlines a method for determining this pH. Minor and Blaisdell<sup>146</sup> criticize Chase's paper and present data which would indicate that there is no direct relation between the pH of white water and that of the distilled water extract of the finished paper, except under special conditions open to variations for each mill and each type of paper. DeCew<sup>144</sup> has determined the adverse effects of gases in the manufacture of paper.

Weber and Snyder,<sup>147</sup> in the laboratories of the Bureau of Standards, have published much data on the relation of lithographic papers to variations in atmospheric humidity and temperature. They find that the moisture content of these papers is influenced by relative humidity, temperature, and the history of conditioning. Humidity changes are the most important. The usual sizing materials have little influence on the moisture content response of paper to changing relative humidity, except with respect to the rate. The relation of sheet properties to register in offset lithography has been discussed by Weber.<sup>148</sup> Trial printings of three groups of special papers made in different mills from different pulps lead to certain conclusions in regard to the use of chemical wood papers from multi-color offset printing. These conclusions may be summarized by saying that desirable paper should have low machine direction coefficient of linear expansion. This is lowest when the greatest number of fibers are parallel to the machine direction and the hydration at a minimum which can be controlled in the mechanical treatment of the fibers.

Wehmhoff<sup>149</sup> discusses the work of the Ink Resistance TAPPI Subcommittee regarding methods for evaluating the printing quality of paper. The committee recommends the adoption of density, oil penetration, oil absorption, and printing smoothness as tentative TAPPI standard tests.

**Pulp Testing.** Morgan<sup>150</sup> has compared the action of a number of milling equipments such as have been proposed for strength testing of pulp. Simmonds and Baird<sup>151</sup> have determined some of the variables in processing pulp in a pebble mill, in a rubber surfaced ball mill, and in a beater. A detailed comparative study of five different sheet machines for pulp evaluation is presented by Doughty and Curran.<sup>152</sup> Williams<sup>153</sup> describes a new, rapid pulp and paper testing outfit, and Green<sup>154</sup> outlines the defects in the design of the sheet-forming device specified by the TAPPI tentative standard T205m and compares this instrument to his own standard sheet mold.

Kress and Brainerd<sup>155</sup> have fractionated a series of chemical and mechanical pulps and the isolated fractions have been tested for chemical and physical properties. They conclude that chemical and physical properties grow poorer in successively shorter fractions of unbeaten chemical pulps, while the strength of mechanical pulps increases with decreasing fiber lengths. They have also investigated the effect of beating on the nature of the fractions from chemical pulps. The conclusions were that in the case of bleached pulps the resistance of pulps to cutting action appears to be related to the purity of the pulps.

**Physical Testing of Paper.** The advent of the N. R. A. and the subsequent establishment of the Paper Industry Authority with its Central Grading Committee resulted in a very considerable activity in the field of physical testing of paper. The subject of specifications and tests and their application to grading has been considered in papers by Mahler,<sup>156-158</sup> Strange,<sup>159-161</sup> Heritage,<sup>162</sup> Carruth,<sup>163</sup> Krimmel,<sup>164</sup> Briggs,<sup>165</sup> Annis,<sup>166</sup> Stuart,<sup>167, 168</sup> Plumstead,<sup>169</sup> Wriston,<sup>170</sup> Boyce,<sup>171</sup> Bullock,<sup>172</sup> and Addoms.<sup>173</sup>

The adoption of optical methods for evaluating paper characteristics in code grading has stimulated a large amount of work, and a number of papers relating to optical methods for testing paper are worthy of note in a survey such as this one. Lewis,<sup>174, 175</sup> Michaelson,<sup>176</sup> Davis,<sup>177</sup> Hunter,<sup>178</sup> and Judd<sup>179</sup> describe various methods for measuring the brightness and whiteness of paper. By means of one of these instruments, the General Electric Reflectometer, Laughlin and Kress<sup>180</sup> have studied the effect of variables encountered in the manufacture of paper on the brightness of the sheet. They conclude from mill studies that the paper machine itself presents no difficulty in regard to brightness control. Variations produced by tub sizing and calendering are likewise practically negligible. The control of brightness appears to be dependent largely upon the uniformity of raw materials and upon the filler content.

The question of the measurement of gloss likewise has received considerable attention and Hunter<sup>181, 182</sup> and Kress and Morgan<sup>183</sup> write regarding new instruments for measuring the gloss of paper. The instrument which has been described by the latter, the Oxford Gloss-meter, possesses distinct advantages over the polarization glarimeter since it is very little effected by color, brightness, and type of coating.

The subject of the measurement of opacity has likewise been gone into rather thoroughly by Judd.<sup>184-186</sup> Dodge and Tarvin<sup>187</sup> show that the printing quality of newsprint is primarily a function of smoothness, absorptiveness, and opacity. Instruments are described for measuring these characteristics. Davis, Roehr, and Malmstrom<sup>188</sup> have described a photoelectric formation tester and Williams<sup>189</sup> a finish and formation tester. A number of papers have also appeared relating to the more common types of physical testing of paper. Monnberg<sup>190</sup> considers critically the probable error and accuracy of testing. Carson<sup>191</sup> writes of the maintenance, calibration, and use of paper testing instruments, and in a second paper<sup>192</sup> describes the whole problem of the scope of paper testing.

New or revised TAPPI methods have appeared, including a tentative revision of method T402m,<sup>193</sup> "conditioning paper for testing," a tentative revision of T400m,<sup>194</sup> "sampling paper for testing," and a tentative revision of T410m,<sup>195</sup> "basis weight of paper." TAPPI committee reports include that of the sub-committee on physical tests of paper as presented by Clark<sup>196</sup> and Scribner's report<sup>197</sup> for the paper testing committee.

Reports have also appeared on the measurement of other characteristics of paper such as the water resistance of paper and fiber board by Carson,<sup>198</sup> a sizing test by Cobb and Lowe,<sup>199</sup> air permeability by Carson,<sup>200, 201</sup> the moisture vapor transmission by Tressler and Evers<sup>202</sup> and Charch and Scroggie,<sup>203</sup> water absorbency by Reese and Youtz,<sup>204</sup> and oil and varnish penetration by Albert.<sup>205</sup>

Methods for studying the stiffness, rigidity, and softness of paper are described by Minor and Minor<sup>206</sup> and Clark.<sup>207</sup> A Gurley stiffness tester has also been described.<sup>208</sup>

Several papers on the manufacture and properties of fiber board have appeared. Arnold<sup>209</sup> has applied the distillation method for the determination of moisture and consistency in the manufacture of insulating board. Arnold and Gleaves<sup>210</sup> have added zinc chloride to insulating board in order to retard attack by mold and insects. A method for counting the plies in solid fiber board has been developed by Baechler.<sup>211</sup> Whittemore, Overman, and Wingfield<sup>212</sup> describe an electrical conductivity method for following the drying of board in the hot press. Jahn<sup>213</sup> outlines tests carried out on fiber board.

**Chemical Testing of Paper.** A number of critical papers on the various methods for the chemical testing of pulp and paper have appeared. Bump<sup>214</sup> has determined the effect of variation in the alkaline solution and the time of treatment on the alpha-cellulose deter-

mination. The effect of the removal of extraneous materials by the pre-treatment of wood on the lignin determination has been investigated by Ritter and Barbour.<sup>215</sup> Hendrickson and Benson<sup>216</sup> have used the determination of lignin as a method for measuring the degree of cooking.

The TAPPI Non-Fibrous Materials Testing Committee<sup>217</sup> has approved a method for the analysis of rosin. The proposed revision of the official TAPPI method for the determination of the amount of coating of mineral coated paper has been described, as approved by the TAPPI Paper Testing Committee.<sup>218</sup> That same Committee has also proposed a tentative standard testing method for the determination of acid-soluble iron in paper.<sup>219</sup> The analysis of paper for titanium pigment is outlined by Jarmus and Willetts.<sup>220</sup> Methods for the determination of bleach demand are described by John and Poppe<sup>221</sup> and by Seborg.<sup>222</sup> The determination of the bleach requirement of pulp by means of its permanganate number is outlined by Wiles.<sup>223</sup> Hughes and Acree<sup>224</sup> describe the quantitative estimation of furfural with bromine, which has an application in the determination of pentosans in pulp and paper.

**Fiber Identification of Structure.** Graff writes in detail on the estimation of fibers in pulp or paper. He<sup>227</sup> goes into the nature of the factors involved in the accuracy of fiber analysis. Other papers<sup>225, 226</sup> take up new stains for fiber evaluation, which stains apply in the differentiation of a number of the new types of fibers now appearing in paper. Kantrowitz and Simmons<sup>228</sup> discuss the relative merits of the commonly used methods for the determination of bleached and unbleached fibers in pulp and paper. Calkin<sup>229</sup> calls attention to the importance of using standard dyes in stains for the differentiation of fibers. Harrar and Lodewick<sup>230-232</sup> present a detailed series of papers relating to the identification and microscopy of woods and wood fibers such as are used in the manufacture of pulp.

Changes in the structure of wood fibers during cooking and bleaching are described by Carpenter and Lewis.<sup>233</sup> The article has been supplemented by a number of cinephotomicrographs in which the swelling analysis has been used to demonstrate the changes which take place in the structure of fibers as the result of degradation.

Ritter<sup>234-236</sup> has continued his work on the microscopic structure of cellulose fibers. In addition to presenting a review of existing material on this subject, he has outlined new evidence on the behavior of fibers during the processing of pulp previous to its manufacture into paper and the relation between this behavior and the inter-fibrillar material. Measurements on the internal and external swelling of wood fibers show that a substantial part of the swelling is internal.

Sisson<sup>237</sup> has continued his x-ray study of the crystallite orientation in cellulose fibers. He explains his latest results with natural fibers on the assumption that a definite discontinuity of crystal structure exists in the concentric layers of cellulose in the cell wall.

**Slime and White Water Problems.** The production of parchment-like membranes from pulp and paper mill slimes deposited upon a sheet-forming substratum and treated with glycerol and mineral oil is described by Sanborn.<sup>234</sup> The slime particles appear to have highly adhesive properties and suggest a probable application as binding and cementing agents. The same author<sup>239</sup> has described factors which are involved in slime control in the mill. Holderby and Warrick<sup>240</sup> have made a pollutional waste survey of Wisconsin pulp and paper mills and have compared these findings to those of previous years. They find that average fiber losses materially increased during 1934.

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## Chapter XXII.

### Synthetic Plastics.

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In view of the fact that the last review of Synthetic Plastics appeared in Volume 7 for the year 1932, this present survey includes the years 1933, 1934, and 1935. The material selected for discussion in this chapter includes all synthetic compounds of a plastic or semi-plastic nature with the exception of the cellulose esters and ethers. These compounds are commonly designated by the term "Synthetic Resins."

Two excellent reviews<sup>1, 2</sup> of the chemistry of these resins have been published during the period in question, and this subject has been exhaustively covered in two volumes published by Ellis<sup>3</sup> in 1935. Nevertheless, the actual progress in the chemistry of synthetic plastics has been reflected to a much greater extent in the patent literature than in any of the scientific journals. Therefore, it is from the former source that most of the information recorded in this chapter was derived.

The synthetic production of resinous materials is practically always accomplished by either of two general classes of chemical interactions; namely, polymerization and condensation. It is under these headings that the developments during the past three years will be discussed. Sometimes both types of reaction are involved as when an already polymerized substance condenses with some other material.

#### POLYMERIZATION

The term "polymerization," as it is used in this review, comprehends those processes in the course of which a more or less considerable number of similar molecules unite to form larger complexes. The degree of polymerization is influenced by the nature of the unsaturated linkages and the substituent groups adjacent to these linkages, by heat, by light, by pressure, and by the presence or absence of a great variety of catalysts. All of these factors will be discussed in connection with the various groups listed below.

**Compounds With a Triple Bond ( $-\text{C}\equiv\text{C}-$ ).** Acetylene ( $\text{CH}:\text{CH}$ ) is capable of polymerization under certain conditions

with the formation of products with a definite resinous character. There is a certain amount of danger inherent in this reaction, because of the possibility of forming compounds of an explosive nature. Calcott and Downing<sup>4</sup> have discovered that the formation of explosive compounds during the polymerization of acetylene was inhibited by performing the reaction in an inert medium, such as nitrogen. A catalyst<sup>5</sup> for producing polymers from acetylene has been formed from materials including a cuprous salt, such as cuprous chloride, and an ammonium salt, such as ammonium chloride, together with a non-aqueous solvent for the cuprous salt, such as ethyleneglycol. In a study of the efficiency of carbon dioxide as a radiochemical catalyst for the polymerization of acetylene,<sup>6</sup> it was determined that only 30 percent of carbon dioxide ionization was used in promoting the reaction.

Methylacetylene ( $\text{CH} : \text{CCH}_3$ ) has been polymerized to a white solid by exposure to ultra-violet light.<sup>7</sup>

The polymerization of vinylacetylene ( $\text{CH}_2 : \text{CHC} : \text{CH}$ ) has been investigated by members of the Du Pont organization.<sup>8-11</sup> It was shown that vinylacetylene can undergo at least three distinct types of polymerization as follows:

Type	Catalyst	Resultant Polymer
A	Cuprous chloride	Acetylene tetramer ( $\text{CH}_2 : \text{CHC} : \text{C}-\text{CH} : \text{CHCH} : \text{CH}_2$ )
B	None	Cyclobutene derivative ( $\text{CH} : \text{CCH}-\text{CHC} : \text{CH}$ )
		$\begin{array}{c}   \qquad   \\ \text{CH}_2-\text{CH}_2 \end{array}$
C	Acids	Styrene ( $\text{C}_6\text{H}_5\text{CH} : \text{CH}_2$ )

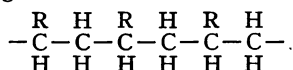
It was inferred that the higher polymers had polycyclobutene-cyclobutane structures. Divinylacetylene has been partially hydrogenated in the presence of a nickel catalyst and the resulting product was polymerized by heating in the presence of benzoyl peroxide to obtain a product of good stability to light.

Halogen derivatives of vinylacetylene were also polymerized.<sup>12, 13</sup> 2-Iodo-1-vinylacetylene ( $\text{CH}_2 : \text{CHC} : \text{CI}$ ) formed a hard resin-like mass which deflagrated when struck, emitting iodine vapor and clouds of heavy brown smoke. The polymerization of 1-halo-2-vinylacetylenes could be accelerated by ultra-violet light, benzoyl peroxide, or ozonides. Chloro-, bromo-, and iodo-polymers have been prepared. The chloro derivative formed the least explosive polymer.

Porous materials such as cloth, paper, or wood have been impregnated with derivatives of vinylacetylene and the material was then subjected to superatmospheric pressure to cause polymerization of the occluded compound.<sup>14</sup> Other products suitable for the impregnation of paper, as well as for the manufacture of safety glass,

have been obtained by the polymerization of vinyl ethynylcarbinol [ $\text{CH}_2:\text{CH}(\text{CH}:\text{C})\text{CHOH}$ ] in the presence of suitable catalysts.<sup>15</sup>

**Compounds With a Single Double Bond ( $-\text{CH}=\text{CH}-$ ).** Polymers of vinyl esters, such as the chloride and acetate, have become important factors in the synthetic resin industry and have consequently been the subject of considerable study. The mechanism of the polymerization was first investigated by Staudinger in 1927 and, according to the review published by Allen, Meharg, and Schmidt<sup>2</sup> in 1934, the following structure is quite generally ascribed to the polymers (R denoting the chloride or acetate radical):



Morrison and Shaw<sup>16, 17</sup> have investigated the catalysts and conditions influencing the formation of vinyl acetate and ethylidene diacetate from the direct combination of acetylene and acetic acid. The progress of the photopolymerization of vinyl acetate has been followed by a determination of the iodine number with Wijs solution.<sup>18</sup> Vinyl chloride and vinyl acetate have been conjointly polymerized<sup>19</sup> with the aid of various catalysts, notably peroxides. In one case<sup>20</sup> acetyl benzoyl peroxide has been directly formed in the reaction mixture by passing dry air or oxygen through a mixture of benzene and acetic anhydride. In addition to the peroxides, a catalyst-assisting material,<sup>21</sup> such as lead, tin, or aluminum, has been used. A polymerized mixture of vinyl chloride and vinyl acetate has been made more resistant to the influence of heat and exposure<sup>22</sup> by including in the reaction a small proportion of hexamethylenetetramine. Polymerized mixtures of vinyl chloride and vinyl acetate have been fractionated<sup>23</sup> by treating them with selected solvents in which the desired fractions were insoluble. The polymerized mixture has been obtained in the form of a molding powder<sup>24</sup> by dissolving it in acetone, treating the solution with ammonia of at least 5 percent concentration with rapid agitation, and then precipitating a powder by adding hydrochloric acid.

The polymerization of vinyl esters and similar unsaturated compounds has been accomplished under the influence of extremely high pressures, such as 2000 to 12,000 atmospheres.<sup>25</sup> The fusibility and solubility of the polymerized esters has been diminished<sup>26</sup> by precipitating them from solution in the presence of an aqueous solution of alkali, whose strength was not sufficient to cause appreciable hydrolysis of the resin. Low viscosity vinyl polymers have been obtained<sup>27</sup> by polymerizing the acetate and the chloride in the presence of an acid whose deleterious action is counteracted as much as desired by the addition of ethylene oxide. The characteristics of the vinyl ester polymers have been further modified by the

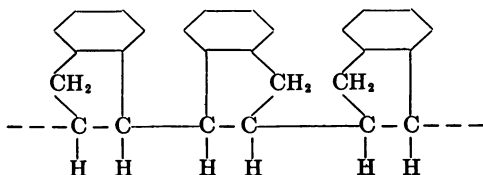
presence of rubber,<sup>28</sup> rosin or a rosin ester,<sup>29</sup> ester gum and drying oils such as linseed oil or China-wood oil.<sup>30, 31</sup>

Various applications of the polymerized vinyl acetate and chloride have been proposed. A solution of polyvinyl acetate in ethyl lactate has been used as a varnish for new and old paintings.<sup>32</sup> Vinyl resins have been used for phonograph records,<sup>33, 34</sup> for dentures,<sup>35</sup> for protective coatings,<sup>36, 37</sup> and for the impregnation of paper<sup>38</sup> and fabrics.<sup>39</sup>

Vinyl compounds other than the acetate and chloride have also been studied. A substantially chlorine-free resin has been obtained by reacting vinyl chloroacetate with an alkali metal salt of an alcohol, phenol, or carboxylic acid and polymerizing the resultant product.<sup>40</sup> Divinyl ether has been polymerized to a highly viscous, resinous material by heating it at 70 to 150° C. for 20 to 24 hours.<sup>41</sup> A product suitable for use in lacquers and in molded products has been obtained by heating vinylnaphthalene to below its decomposition point (i.e., about 300° C.).<sup>42</sup>

Styrene (vinylbenzene) is capable of polymerization with the formation of hard glass-like resins. These resins have found numerous applications in industry. Houtz and Adkins<sup>43</sup> have followed the course of the polymerization of styrene by determinations of the viscosity of the solution, and the weight and specific viscosity of the resultant polystyrene. The polystyrene chains of greatest length, as measured by the specific viscosity, were formed in an atmosphere of nitrogen at 110° C. Certain peroxides (especially diisobutylene ozonide) were much more active catalysts than ozone. Crude styrene has been polymerized by heating it in the presence of benzoyl peroxide formed *in situ* from ozone and benzene.<sup>44</sup> Styrene will even polymerize in the absence of ozone but at a diminished rate.<sup>45</sup> Polystyrene, after precipitation and drying, retained its capacity to add more styrene with the formation of chains of greater length. Polymerized styrene<sup>46</sup> has been found particularly suitable for making acoustic diaphragms such as those of telephone transmitters and microphones.

Those resins obtained by the polymerization of indene and of cumarone have been known for many years. The structure of polyindene has been represented as follows:<sup>1</sup>



The structure of polycumarone is similar with an —O— replacing the —CH<sub>2</sub>— group.

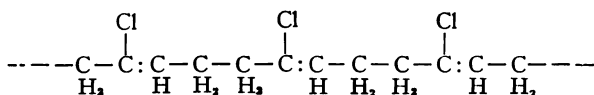
A recent patent<sup>47</sup> stated that cumarone may be polymerized, with the aid of a catalyst such as sulfuric acid, in the presence of a liquid diluent, such as a petroleum fraction which is inert to the polymerizing reaction and is a solvent for the resulting resin but a non-solvent for the catalyst. In the formation of resins of the cumarone-indene type, polymerization of the initial materials has been effected in the presence of an absorbent earth, such as fuller's earth, and an acid ferric sulfate.<sup>48</sup>

Acrylic acid ( $\text{CH}_2\text{:CHCOOH}$ ) and its derivatives have been transformed by polymerization into very interesting resins, many of them of a hard, colorless, glass-like nature. However, most of the recent investigations along this line have been carried out in countries other than the United States. One recent United States investigation<sup>49</sup> has revealed that a bubble-free polymer of an acrylic or alkacrylic acid may be obtained by heating it until the temperature of at least some portion of the mass approaches the temperature of bubble formation, then cooling until the reaction is substantially stopped and again heating and cooling alternately. Compositions for the production of sound-records<sup>50</sup> have been produced from thermoplastic resins obtained by the polymerization of acrylic acid, alkacrylic acid or their esters, nitriles, or amides.

Polymerization products of esters of ethylenedicarboxylic acids, such as fumaric, maleic, citraconic, and mesaconic acids,<sup>51</sup> have been used conjointly with polymerized vinyl esters or styrene.

**Compounds With Conjugated Double Bonds.** The polymers of unsaturated organic compounds of this class are distinguished by the fact that they are more rubbery than resinous. The most important member of this group is Chloroprene, chemically designated as 2-chloro-1,3-butadiene ( $\text{CH}_2\text{:CClCH:CH}_2$ ), whose polymer, Duprene, has been developed by E. I. du Pont de Nemours & Company as a substitute for rubber. The basic patents on the preparation and polymerization of the chlorobutadienes were issued in March, 1934.<sup>52</sup>

The structure of polychloroprene has been represented as follows:<sup>1</sup>



Williams and Walker<sup>53</sup> have studied the effect of oxygen and water on the polymerization of Chloroprene. They concluded that oxygen increased the rate of polymerization of Chloroprene, but that it was not necessary for either the polymerization to  $\alpha$ -polychloroprene or for the conversion of  $\alpha$  to  $\mu$ -polychloroprene during vulcanization. The rapid polymerization in emulsions was due to the nature of the polar interfaces and to their distance apart rather than to the increased surface of accelerating action of the dispers-



ing agent. In the commercial application of the Chloroprene plastic polymer,<sup>54</sup> the scorching of this polymer has been guarded against by mixing it with a plastic, elastic reaction product of an aromatic compound, such as benzene, with ethylene chloride.

In the polymerization of the related compound, 2-methyl-1,3-butadiene ( $\text{CH}_2:\text{C}(\text{CH}_3)\text{CH}:\text{CH}_2$ ), commonly known as isoprene, an insoluble polymer was largely formed when the aluminum chloride catalyst was in the solid state. When the aluminum chloride was put in solution as a complex in the isoprene, a soluble polymer was largely formed.<sup>55</sup> The homogeneous thermal polymerization of isoprene has been investigated in the temperature range of 286.5 to 371° C. at pressures ranging from 212 to 739 mm.<sup>56</sup>

The chlorine derivatives of butadiene have been the subject of exhaustive studies.<sup>57</sup> The polymerization of 2,3-dichloro-1,3-butadiene was inhibited by hydroquinone and accelerated by air or benzoyl peroxide. The polymer was an opaque, tough, hard mass, non-plastic and lacking in extensibility. 1,2,3-Trichloro-1,3-butadiene polymerized very slowly to form a dark-colored, rather soft and friable mass. The speed of spontaneous polymerization of the chlorobutadienes was graded as follows: 2,3- $\gg$  2- $\gg$  1,2,3- $>$  1- $\gg$  1,2,3,4-chloro. Only the second member of the series (Chloroprene) yielded a definitely rubber-like polymer.

The preparation and polymerization of other butadiene derivatives has been reported by Coffman<sup>58</sup> and Dykstra.<sup>59</sup> Among those studied were 4-cyano-1,3-butadiene and the oxyprenes, 2-ethoxy-1,3-butadiene and 2-butoxy-1,3-butadiene. As substitutes for rubber the polymers of these oxyprenes were inferior to polychloroprene.

The polymerization of unsaturated organic compounds with conjugated double bonds has been studied by Starkweather<sup>60</sup> at pressures ranging from 2000-9000 atmospheres and temperatures ranging from 20 to 74° C. At about 6000 atmospheres an increase of 1000 atmospheres doubled the rate of polymerization. The rate was increased by substituent groups in the  $\beta$ - or 2-position in the order alkyl, phenyl, chlorine, bromine, iodine. In the  $\alpha$ - or 1-position, halogens were less effective and alkyl groups were inhibitory.

Werntz<sup>61</sup> has investigated the addition of organic carboxylic acids to vinylacetylene. Acetic acid reacted with vinylacetylene in the presence of a catalyst, such as a mercury salt or boron fluoride, to give 1,3-butadienyl-2-acetate. The corresponding formate, chloroacetate and butyrate were similarly formed. These esters were polymerized under normal conditions or under high pressure or in emulsions, with the formation of a rubber-like material. Unlike Chloroprene, the acetate, when polymerized under the influence of peroxide catalysts, yielded resinous products.

A product which was suitable for coating compositions has been

produced by heating furylethylene in the presence of a catalyst such as benzoyl peroxide and discontinuing the heating before the polymer became insoluble in toluene.<sup>62</sup>

**Mixtures of Olefins and Diolefins.** The polymerization of mixtures of unsaturated hydrocarbons obtained from cracked petroleum distillates was first reported by Thomas and Carmody in 1932.<sup>63, 64</sup> The resins obtained in this manner offered possibilities for use in varnishes and were of particular commercial interest because of their low cost.

These mixtures of unsaturated hydrocarbons have been polymerized by heating at 25 to 35° C. in the presence of aluminum chloride as a catalyst,<sup>65</sup> and also in conjunction with an alkyl benzene, if so desired.<sup>66</sup> Unsaturated components of cracked petroleum distillates boiling below 230° C. have been polymerized to products boiling at 300° C. or higher and oils of lower boiling point were then separated from the polymers.<sup>67</sup> Compounds transparent to light in a layer thickness of 2 inches and having drying properties equal to vegetable oils have been prepared by fractionating unrefined vapor-phase cracked gasoline and polymerizing the lighter condensable fraction having a boiling point not over 112° C.<sup>68</sup> An oil such as a crude coal-tar naphtha has been heated with lead oxide, then distilled and treated with a polymerizing agent, such as sulfuric acid, to obtain light-colored varnish resins.<sup>69</sup> Resinous material has been formed from petroleum sludge by heating the sludge and treating it with sodium chlorate or other similar agent.<sup>70</sup>

#### Unsaturated Linkages With Elements Other Than Carbon.

Lactide ( $\text{CH}_3\text{CH} < \begin{smallmatrix} \text{OCO} \\ \text{COO} \end{smallmatrix} > \text{CHCH}_3$ ) has been polymerized by heating it at temperatures ranging from 250° C. to a temperature approaching that at which decomposition of the polymerized product began to occur. The polymerized product was further heated within this temperature range and at a pressure below 100 mm. of mercury, in order to remove monomeric lactide by distillation.<sup>71</sup>

It has been reported that bromoalkyldimethylamines polymerize readily to give products which are hygroscopic and vary in physical state from resinous gums through glass-like products to amorphous solids.<sup>72</sup>

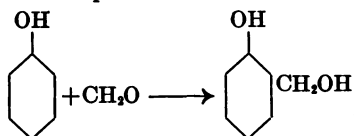
#### CONDENSATION.

The term "condensation," as used in this review, distinguishes those polymerization processes, usually involving two or more compounds, in which there is a separation of some substance, such as water, as a by-product of the reaction. Within the wide limits of this definition, condensation includes those processes ordinarily described as esterification, etherification, lactone and anhydride formation, oximation, etc. As in the case of straight polymeriza-

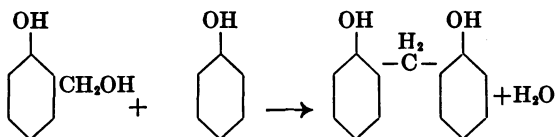
tion, condensation is promoted by a great variety of catalysts, as is indicated in connection with the various groups listed below.

**Phenol With Formaldehyde.** The mechanism of the phenol-formaldehyde condensation has been the subject of considerable study ever since Baekeland developed this reaction on a commercial scale. In the excellent review of this work by Allen, Meharg, and Schmidt,<sup>2</sup> the great variety of reactions possible between phenol and formaldehyde either in neutral, acid, or alkaline solutions, and either with phenol or formaldehyde in excess, are represented by the following equations:

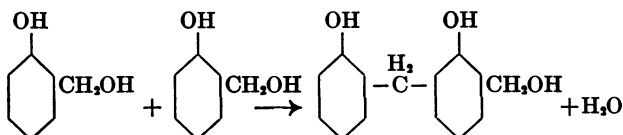
(a) Alkaline reaction = phenol alcohol



(b) Alkaline or acid reaction = Novolak



(c) Alkaline reaction = Resol (Bakelite A)



(d)  $x\text{Resol} + y\text{Resol} = \text{Resit (Bakelite C)} + \text{water}$

(e)  $x\text{Novolak} + y\text{ formaldehyde} = \text{Resit} + \text{water}$

If the reactions represented by equations (a) and (b) are considered as a unit, one molecule of phenol has reacted with 0.5 molecule of formaldehyde. As the ratio approaches 1 to 1 the chains which constitute the Novolak become longer, resulting in a resin of higher melting point, of lesser solubility in caustic or alcohol, and finally of complete infusibility and insolubility as the 1 to 1 limit is reached.

In the limited space of this review it is possible to give only a brief summary of the developments in the phenol-formaldehyde resins during the years 1933, 1934, and 1935. The initial condensation of phenol with formaldehyde has been performed in the presence of strong alkaline catalysts, such as sodium hydroxide and potassium carbonate, and the reaction mixture has then been

neutralized by such acids as sulfuric, hydrochloric,<sup>73</sup> lactic,<sup>74</sup> tartaric,<sup>75</sup> or succinic.<sup>76</sup> In certain cases the entire condensation has been carried out in an alkaline medium, e. g., in the presence of aniline,<sup>77, 78</sup> ammonia,<sup>79</sup> hexamethylenetetramine,<sup>80</sup> triethanolamine, or trisodium phosphate.<sup>81</sup> The condensation has been halted at the desired stage by running the condensate directly into water to form a suspension<sup>82</sup> or by the addition of a relatively cold solvent, whose boiling point is above 100° C., such as butyl alcohol or amyl acetate.<sup>80</sup> The condensation products have been freed from uncombined phenol by distillation at a temperature of 140° C. or higher in the presence of high-boiling non-resinous organic fluxing compounds such as glycerol, ethyleneglycol, or phthalic esters.<sup>83</sup> Transparent phenol-formaldehyde resins have been formed by adding to the condensation a decolorizing agent consisting of a mixture of acetic acid, camphor, glycerol, and hydrochloric acid.<sup>84</sup> The condensate has been hardened while it was still liquid and hot by adding a slight excess of oxalic or phosphoric acid.<sup>85</sup> Products of high brilliancy have been obtained by the addition to the partially condensed mixture of about 0.5 percent of an oxidizing agent, such as ammonium chromate or potassium permanganate.<sup>86</sup>

The phenol-formaldehyde condensates have been modified for coating purposes by including in the condensation certain oils such as linseed oil<sup>87, 88</sup> wood oil,<sup>89</sup> or tung oil,<sup>90</sup> as well as certain natural resins, such as rosin<sup>91</sup> or the glycerol ester of a natural resin acid.<sup>92</sup> A resin which may be hardened by heating has been formed from phenol, formaldehyde, and an alkyl ester of citric acid which served as a plastifier.<sup>93</sup> Oil-soluble synthetic resins have resulted from the condensation of phenol and formaldehyde with bis-(4-hydroxyaryl) dialkylmethane ketone.<sup>94</sup> Tests have been described in which a part of the linseed oil in typical house paints was replaced with tung oil-phenolic resin varnishes. After over 2 years exposure the indications were that weathering would result in chalking rather than checking or cracking.<sup>95</sup> It has been determined that the hardness and speed of drying of phenolic-resin varnishes were proportional to the melting point of the resin.<sup>96</sup> Varnishes must be free from the initial condensation products of phenol and formaldehyde.<sup>97</sup> For varnishes, the non-heat-hardening type of phenolic resin has been found superior to the heat-hardening type, in that the former is susceptible to better control during cooking and to less yellowing.<sup>98</sup>

The adaptation of phenol-formaldehyde condensation products to molding compositions has received considerable attention in the period covered by this review. The phenolic resins have found continued use as binders in the production of toothed gears,<sup>99, 100</sup> threaded caps,<sup>101</sup> and large plant equipment where resistance to acid was desired.<sup>102</sup> The resinous binder has been incorporated

with fillers, such as asbestos, mica,<sup>103, 104</sup> wood flour,<sup>105, 106</sup> and fabrics of various kinds. A molding composition has been formed by including barium phenoxide in the reaction mixture and then incorporating a filler in the condensate.<sup>107</sup> Bakelite resinoid has been used as a mounting medium for small metallographic specimens and metal powders.<sup>108</sup> The molded Bakelite products have been of considerable interest for electrical insulation. Fibrous material, such as paper, has been impregnated with the resinous condensate to form a product suitable for electric insulation.<sup>109</sup> The electrical conductivity, dielectric strength, direct-current resistance and power factor of various types of Bakelite materials have been determined. It has been shown that all three tests were required to describe completely the electrical properties of these resins.<sup>110, 111</sup>

**Phenolic Mixtures with Formaldehyde.** In many cases it has been found expedient to substitute in place of the purified phenol, certain cruder mixtures containing phenol as one constituent. Formaldehyde has been condensed with "phenol oil",<sup>112</sup> crude cresylic acid,<sup>113, 114</sup> and with a low-temperature coal tar distillate either in an acid,<sup>115</sup> or alkaline solution.<sup>116-120</sup> In one modification of this process, an intermediate phenol-formaldehyde resin was treated with the addition of an alkaline solution of the high-boiling tar acid components of a low-temperature coal tar together with at least a molecular equivalent of formaldehyde.<sup>121</sup>

Resinous compositions substantially not penetrable by short-wave rays, such as x-rays or radium rays, have been prepared by the condensation of an aldehyde with a phenolic compound of lead, uranium, thallium, or thorium.<sup>122</sup>

**Homologues of Phenol with Formaldehyde.** Formaldehyde has been condensed with a dihydroxybenzophenone to form a synthetic resin compatible with cellulose esters<sup>123</sup> and with *m*- and *p*-cresols in the presence of a coal tar acid containing a substantial amount of xlenol.<sup>124</sup> A xlenol-formaldehyde-magnesium oxide resin has been formed by heating and by vacuum drying. This resin softened but did not flow on a hot plate at atmospheric pressure, whereas it flowed freely and set to a hard mass when hot-pressed at about 165° C.<sup>125</sup> Resorcinol-formaldehyde resins have been found suitable for sound records. They may be plasticized with rape-seed oil<sup>126</sup> or modified by adding to the condensation cresol in which *p*-nitraniline is dissolved.<sup>127</sup> They have also been emulsified by the use of beeswax in the presence of an alkaline salt such as borax.<sup>128</sup>

Oil-soluble resins have been prepared by condensing formaldehyde with thymol,<sup>129</sup> *p*-*tert*-butyl- or amylphenol,<sup>130</sup> *o*-crotyl- or allylphenol,<sup>131</sup> *p*-cyclohexylphenol,<sup>132</sup> *o*- or *p*-hydroxybiphenyl,<sup>133</sup> xlenol<sup>134</sup> or a neutral alkyl ether of xlenol.<sup>135</sup> The condensates were readily soluble in tung oil and permitted the preparation of

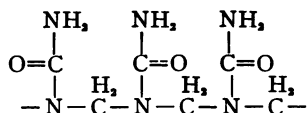
varnishes which dried rapidly to films highly resistant to moisture, alkalis, and sunlight.

**Phenol with Aldehydes, Ketones and Carbohydrates.** Phenol has been condensed with paraldehyde in the presence of an acid catalyst<sup>136</sup> and with furfural in the presence of an alkaline condensing agent.<sup>137-139</sup> Condensation products suitable for use with nitrocellulose lacquers have been produced by heating phenol with benzoyl-*o*-benzoic acid in the presence of sulfuric acid.<sup>140</sup> Phenol has been condensed with ketones such as acetone<sup>141</sup> or  $\alpha$ -chloroacetone<sup>142</sup> to form products compatible with cellulose derivatives. Phenol has been reacted with formaldehyde and a ketone, such as acetone or cyclohexanone, in the presence of an alkaline catalyst to form an elastic resin which was readily hardened by heat and was not darkened when heated at 180° C.<sup>143</sup>

A water-soluble synthetic resin has been produced by condensing phenol and formaldehyde with an alkaline solution of sucrose and terminating the reaction before the product became insoluble.<sup>144</sup> A primary carbohydrate-phenol resin has been heated to about 230° C. with the addition of glycerol to form a product which was substantially infusible.<sup>145</sup> A coating composition comprised a carbohydrate-phenol reaction product and a metal oxide or hydroxide in a volatile solvent together with a reactive hardening agent such as hexamethylenetetramine.<sup>146</sup>

**Urea and Thiourea with Formaldehyde.** The condensation products of urea and formaldehyde have been very important as plastics but have not been extensively used in varnishes or lacquers. They are particularly distinguished by their hardness, transparency, and absence of color, and for this reason have been widely heralded as substitutes for glass.

The structure of the urea-formaldehyde polymer has been represented as follows:<sup>2</sup>



The condensation of formaldehyde with urea, like the condensation with phenol, has usually been carried out in several stages. In general the urea was first caused to react with not more than 1.4 mols. of formaldehyde at a temperature of not over 70° C. and additions of formaldehyde were then made with continued heating until the final proportion was about 1.1 to 1.3 mols. of urea for every 2 mols. of formaldehyde.<sup>147-153</sup> An excess of formaldehyde might be used in the beginning and then removed by passing air or steam through the solution before completing the polymerization.<sup>154</sup> The formation of cloudiness has been prevented by adding salts, such as sodium chloride.<sup>155</sup>

The urea-formaldehyde condensation has been carried out in the presence of phthalic anhydride,<sup>156</sup> acetaldehyde,<sup>157</sup> zinc chloride,<sup>158</sup> silica gel,<sup>159</sup> hydrogen sulfide,<sup>160</sup> ferrous sulfide,<sup>161</sup> thiourea,<sup>162</sup> phenol,<sup>163</sup> or a substantially anhydrous alcohol containing an inert dehydrating agent.<sup>164</sup> Superatmospheric pressure has been used to facilitate the condensation.<sup>165, 166</sup> An intermediate condensation product has been preserved in the jelly stage by the addition of a colloidal retarder such as gum tragacanth<sup>167</sup> or gum acacia.<sup>168</sup>

Molding compositions have been obtained by mixing the urea-aldehyde condensation product with water,<sup>169</sup> resorcinol,<sup>170</sup> a natural resin,<sup>171</sup> sulfite fiber,<sup>172</sup> and nitrocellulose.<sup>173</sup> The condensate has been rendered substantially insoluble by heating with an acid, such as salicylic acid.<sup>174</sup> Urea has been mixed in the dry state with a solid polymeric aldehyde (such as paraformaldehyde) and a filler to give a mixture which could be condensed and hardened at the same time by hot-molding.<sup>175, 176</sup> A powder suitable for molded articles was obtained by reacting formaldehyde with ammonium thiocyanate or unaltered dicyandiamide and urea or thiourea.<sup>177, 178</sup> Alternatively, the resinous condensation product of formaldehyde and thiourea has been contacted with an excess of water to precipitate a fine powder suitable for molding.<sup>179</sup>

Solutions suitable for use as a varnish or lacquer have been prepared by dissolving a permanently fusible resin from thiourea and formaldehyde, together with a hardening agent, such as paraformaldehyde, in a mutual solvent, such as ethyl lactate or ethylene-glycol.<sup>180</sup> Water solutions of a thiourea-formaldehyde condensate have been stabilized with ammonia and carbon dioxide to render them suitable for coating various materials.<sup>181</sup>

**Other Amines with Formaldehyde.** Resins which are compatible with cellulose derivatives have been formed by condensing formaldehyde with toluenesulfonamide<sup>182-184</sup> or with ammonium thiocyanate.<sup>185</sup> Products of a resinous character suitable for rust-proofing coatings on metals have been obtained by reacting paraformaldehyde with a phosphorus amide.<sup>186</sup> Formaldehyde has also been condensed with a primary aromatic amine, such as aniline or naphthylamine<sup>187</sup> and with dicyandiamide and a protein material, such as casein.<sup>188</sup>

**Polyhydric Alcohols with Polybasic Acids.** According to Kienle's theory of flexible resin formation,<sup>189</sup> long-chain molecules (heat-nonconvertible) attached through primary valence linkages to heat-convertible resin molecules (such as glyceryl-phthalate) should yield flexible heat-convertible resins. Such resins were prepared by heating together a dihydric alcohol-dibasic acid polyester as the heat-nonconvertible, flexibilizing phase and glyceryl triphthalate as the heat-convertible phase. Since the flexibility of the product depended largely on the mole ratio of the phases, it thus became

possible to produce resins of definite and controlled flexibility by intentional formulation.<sup>190-192</sup>

In commercial practice the glycerol-phthalic anhydride condensation has been modified by the presence of natural glycerides or the fatty acids obtained by hydrolysis of such glycerides. The following oils have formed a source of supply for this purpose: China-wood oil,<sup>193</sup> linseed oil,<sup>194-202</sup> tung oil,<sup>203-205</sup> rubber-seed oil,<sup>206</sup> castor oil,<sup>207, 208</sup> and corn oil.<sup>209</sup> Other modifying agents have been recommended, such as borneol,<sup>210</sup> butanol,<sup>211, 219</sup> rosin,<sup>212</sup> shellac,<sup>213</sup> oleic acid,<sup>214, 215</sup> a ketene,<sup>216</sup> glycerol glutamate,<sup>217</sup> zinc or calcium oxide,<sup>218</sup> and partially esterified glycerides made by treating a drying oil in the presence of water with a hydrolyzing enzyme.<sup>220</sup> A fusible alkyd resin has been rendered infusible by heating it with acetic anhydride or acetyl chloride.<sup>221</sup>

Phthalic acid has been condensed with compounds other than glycerol to produce resinous products, e. g., maleic acid,<sup>222, 223</sup> oleic acid with triethanolamine,<sup>224</sup> and lactic acid in combination with ethyleneglycol.<sup>225</sup> Glycerol has been condensed with compounds other than phthalic anhydride, e. g., bromomaleic anhydride with the monoisopropyl ester of monochlorosuccinic acid,<sup>226</sup> bromomaleic anhydride with acrylic acid,<sup>227</sup> and citric acid.<sup>228</sup>

Alkyd resins have been extensively used for varnishes, either straight, phenol-modified and oil-extended or natural-resin modified.<sup>229-235</sup> They have been used for lacquers in combination with nitrocellulose<sup>236-238</sup> and with cellulose acetate.<sup>239</sup> The question of suitable solvents for these resins has received consideration.<sup>240</sup> High-boiling solvents, such as diethyl oxalate and ethyl lactate, have been recommended for some purposes.<sup>241</sup> Solutions of alkyds in mixtures of xylene and naphtha have been reduced in viscosity by the addition of small amounts of butyl alcohol.<sup>242</sup> The tolerance of toluene solutions for denatured alcohol, ethyl acetate and mineral spirits has been determined. In general the most tolerance was shown for ethyl acetate and the least for alcohol.<sup>243</sup> An oil-modified alkyd resin has been used with a highly volatile solvent to produce a wrinkle-finish coating.<sup>244</sup> Hart and Gardner<sup>245</sup> have noted the tendency of white and light-tinted paints using alkyd vehicles to chalk.

Alkyd resins have also been used for molded products,<sup>246-248</sup> both alone and in combination with urea-aldehyde resins,<sup>249</sup> casein-formaldehyde,<sup>250</sup> and rubber.<sup>251</sup> They have formed the basis of solventless cements whose hardening was accelerated by dehydration catalysts, such as zinc oxide.<sup>252</sup>

Kienle and Race<sup>253</sup> have studied the electrical, chemical, and physical properties of alkyd resins. They pointed out that alkyd resins might be hard, rigid, soft, balsam-like, flexible, or rubbery. During the formation of unmodified alkyd resins, there occurred a progressive increase in electrical resistance with time, the tempera-



ture being kept constant. The observed electrical characteristics of alkyd resins were best explained by the theory of conduction in the solvating component of a gel structure.

**Other Condensations with Separation of Water.** Resinous plastics have been formed by the condensation of aldehydes with guanidine and its homologues,<sup>254</sup> sulfonamides,<sup>255</sup> benzidine,<sup>256</sup> polyvinyl alcohol,<sup>257, 258</sup> cracked hydrocarbon oil distillates,<sup>259</sup> and hardwood tar distillates;<sup>260</sup> also by the condensation of allyl alcohol with cresol in the presence of zinc chloride,<sup>261</sup> of furfural with urea in the presence of China-wood oil,<sup>262</sup> of phenol and *o*-cresol with hexamethylenetetramine,<sup>263</sup> and of alkylolamines with themselves in the presence of an alumina catalyst.<sup>264</sup> Carbohydrates and proteins have entered into resinous condensations: as for example, sucrose or glucose with formaldehyde,<sup>265</sup> pectose with formaldehyde or a ketone,<sup>264</sup> dextrose with maleic anhydride,<sup>265</sup> casein, gelatin, or albumin with glycerol,<sup>266</sup> and corn gluten with formaldehyde and phenol.<sup>267</sup>

**Condensations Involving Sulfur or its Compounds.** Resinous plastics have also been formed by the interaction of divinylacetylene with sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ )<sup>265</sup> and sulfur chloride ( $\text{S}_2\text{Cl}_2$ ),<sup>266</sup> of phenol with sulfur chloride,<sup>267</sup> of cracked hydrocarbon distillates with sulfur,<sup>268</sup> of aldehydes or ketones with a mercaptan,<sup>269</sup> of ethylene dichloride with soluble polysulfides,<sup>270-272</sup> and of aldehydes or furfural with polysulfides.<sup>273, 274</sup>

**Miscellaneous Condensations.** Other plastic forming condensations have included methylene dichloride with sodium phenate,<sup>275</sup> ethylene dichloride with benzenoid hydrocarbons,<sup>276</sup>  $\alpha$ -terpinene or terpinolene with maleic anhydride,<sup>277</sup> pinene with maleic anhydride,<sup>278, 279</sup> cineol with maleic anhydride,<sup>280</sup> pinene with toluene,<sup>281</sup> and trichloroethylene with itself in the presence of aluminum chloride.<sup>282</sup> Abietic acid has formed the basis of synthetic resins which were also suitable for use as plasticizers.<sup>288-291</sup>

## RUBBER DERIVATIVES

The story of recent developments in synthetic plastics would not be complete without mention of the modified-rubber compounds. A chlorinated rubber, marketed under the name of Tornesit, has proved to be a valuable base for coating compositions.<sup>292</sup> Chlorinated rubber is a light yellow solid which has a specific gravity of 1.5.<sup>293</sup> The best solvents for chlorinated rubber are the aromatic hydrocarbons.<sup>294</sup> Suitable plasticizers are the soft alkyds, chlorinated naphthalene, methyl or benzyl abietate, and some synthetic oils.

A new molding resin, called Plioform, has been formed by certain adaptations of the reaction between rubber and the chlorotin acids.<sup>295</sup> This resin is tough, odorless and tasteless, resistant to

alkalies, most acids, and moisture, and is thermoplastic. It is soluble in gasoline or benzene but insoluble in acetone. It is also available in sheet form.

#### SUMMARY

During the period covered by this survey there have been several comprehensive reviews<sup>290-304</sup> which emphasize the important place which synthetic plastics have established for themselves in modern industry, and which point out the probable trends of these developments in the near future.

**Synthetic Plastics for Coatings.** The varnish industry has, in the past few years, undergone a radical change with the introduction of the newer types of phenolic and alkyd resins which are not only oil-soluble but also exert a beneficial influence on the resulting oil-resin coatings. Thus, there have been developed a series of quick-drying varnishes in which the objectionable processes of the drying of siccative oils have been substantially eliminated by uniting the drying element in the structure of the synthetic resin molecule.

Ellis<sup>1</sup> summarizes the present trend of the coating industry as being towards the development of an ideal resinous substance which shall be soluble in cheap solvents, quick-drying, light-colored, flexible, even at low temperatures and highly resistant to heat, water, light, acids, and alkalies. Change to an insoluble form shortly after application is desirable. There should be little or no progressive change upon aging.

**Synthetic Plastics for Molded Articles.** Breskin<sup>298</sup> states that among the present-day molded plastics are a number of applications so common that few think of them as novelties any longer. Heat resistance makes them ideal for radiator knobs. Electrical resistance makes them ideal for switches, plugs, insulators, and other electrical fixtures. Resistance to wear has brought them into favor for door knobs, bell pushes, and various articles of furniture. Their decorative qualities and workability are making them increasingly popular as a building material, particularly in laminated sheets for interior decorative effects.

Molded plastics have also been used for phonograph records, for dentures and for the construction of plant and laboratory apparatus which is distinguished by its acid resistance. Synthetic plastics of the clear, colorless type have been proposed as a substitute for glass for a number of purposes and some appear to have possibilities as the intermediate films in laminated safety glass.

**Other Applications for Synthetic Plastics.** Improvements in grinding wheels have been made by using phenolic resinoids as the binder for the abrasive. Paper has been impregnated with a phenol resinoid and used instead of glue in the production of wood veneers. A flexible waterproof cloth, called Revolite, has been

manufactured by calendering the fabric with a phenolic resinoid. This fabric has been used for surgical tape, raincoats, shower curtains, etc. Special anti-crease fabrics impregnated with the colorless urea resins are coming into increasing prominence. Phenolic resinoids have proved quite valuable in floor-covering compositions of the type of linoleum, and as binders in various brake linings.

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## Chapter XXIII.

### Rubber.

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Chemistry has continued to play a major rôle in the advancement of the rubber industry. Although there have been no spectacular discoveries during the year 1935, hundreds of investigators have been actively applying their chemical knowledge to solve the intricate problems of this major industry.

The executives of the large rubber companies, several of whom served their apprenticeships in the chemical laboratory,<sup>1</sup> appreciate the potentialities of chemical research as evidenced by their generous support of research work and the resulting publications. The government laboratories have also contributed some very important papers. Many suppliers to the rubber industry are maintaining very productive research laboratories and have contributed freely to the literature. One of the suppliers, E. I. du Pont de Nemours & Company, was given the award for chemical engineering achievement for bringing to fruition during the past two years the successful industrial development of synthetic rubber, "DuPrene."<sup>2</sup>

A noteworthy general paper, "Rubber Industry at the Crossroads," was contributed by Geer,<sup>3</sup> who was largely responsible for the awakening of the rubber industry to the value of research. Geer feels that there are two courses open: "either to keep on along present lines or to branch out upon a broad, intense program of fundamental research. Executives must face now the law of diminishing returns in research conducted along present lines. If an ample appropriation were made for a cooperative research laboratory and continued over a period of ten years, the entire scope, quality, and utility of the rubber industry might be revolutionized."

**Crude Rubber.** By a method of total reflection, McPherson and Cummings<sup>4</sup> have determined the refractive index values of rubber in different forms. The average (N. D. 25) values of Hevea crude rubber and purified rubber were approximately the same, regardless of differences in the non-rubber components, nor were the values altered by mastication. The "n" value of crude rubber was not altered by the addition of rubber-insoluble fillers, whereas solu-



ble substances changed the "n" value in proportion to their own "n" values and their proportional weight of the rubber. The "n" value offers a method for determining the solubility of a substance in rubber. Sulfur in rubber increased the  $n_D^{25}$  of crude rubber by 0.0016 for each percent and phenyl- $\beta$ -naphthylamine by 0.0015 for each percent. The combination of a given proportion of sulfur with rubber increased the "n" value more than the solution of the same proportion of sulfur in the rubber, and therefore, when rubber is vulcanized, there is a progressive increase in its "n" value. A formula for finding "n" is given, and the changes in the slope of the curve, plotted with "n" values as a function of the temperature, are discussed.

Forms of rubber as indicated by temperature-volume relationship have been investigated by Bekkedahl.<sup>5</sup> Temperature-volume measurements were made from  $-85$  to  $+85^\circ$  C. on rubber hydrocarbon and three soft rubber-sulfur compounds. Measurements of linear expansion were taken on one specimen of rubber hydrocarbon from  $-190$  to  $0^\circ$  C. These measurements indicate that unvulcanized rubber may exist in at least four forms: amorphous I, crystalline I, crystalline II, and amorphous II. Vulcanized rubber, in the unstretched state, exhibited only the amorphous I and the amorphous II forms. The results of this investigation afford a basis for correlating and interpreting data obtained by the author and other investigators on the heat capacity, electrical properties, and behavior of rubber on stretching.

A method was previously described for purifying the hydrocarbon in Hevea latex and separating it into two fractions by extraction with ethyl ether. The present paper of Smith and Saylor<sup>6</sup> deals with the insoluble (the gel) fraction, of which about 25 percent of the total hydrocarbon is composed. Presumably the gel is insoluble in ether, because of a complex structure and high molecular weight. When traces of oxygen are present, it becomes soluble in suitable organic liquids. The dissolved gel was crystallized from a dilute solution at low temperatures and the crystals were examined. The refractive indices,  $E=1.535$  at  $-5^\circ$  C. and  $W=1.583$  at  $-5^\circ$  C., are very close to the values previously found for crystals of ether-soluble hydrocarbon. Melting temperatures ( $-5$  to  $+14^\circ$  C.) depend upon the history of the sample and indicate that the crystals are solid solutions, probably of many closely related components. As witnessed by micromanipulation below their melting temperature, the gel crystals contrast sharply in elasticity with the crystals of sol rubber. The former appear to be elastic, the latter are plastic. Also, after the loss of birefringence indicates that the crystals are melted, the gel is more resistant to deformation than the sol. Crystals of ether-soluble rubber have been vulcanized below their melting point by means of sulfur chloride. The shape of the crystals

remains unchanged, but birefringence disappears, and their resistance to deformation is increased.

Bekkedahl and Matheson<sup>7</sup> have determined the heat capacity, entropy, and free energy of rubber hydrocarbon. Measurements of heat capacity were made on rubber hydrocarbon in its different forms from 14 to 320° K. At 14° K. the heat capacity was found to be 0.064 j/g/° C. for both the metastable amorphous and the crystalline forms. With increase in temperature, the heat capacity increases gradually up to a transition temperature at about 199° K. At 199° K. both forms undergo a transition of the second order, the heat capacity rising sharply. For the amorphous form above this transition, the heat capacity rises gradually without discontinuity to the highest temperature of the measurements. The crystalline form undergoes fusion at 284° K., the heat of fusion being 16.7j/g. At 298.1° K. the heat capacity of the rubber is  $1.880 \pm 0.002$  j/g/° C. The entropy of rubber at 298.1° K. is  $1.881 \pm 0.010$  j/g/° C. The free energy of formation of rubber from carbon (graphite) and gaseous hydrogen is  $1.35 \pm 0.10$  kj/g.

Jessup and Cummings<sup>8</sup> have investigated heats of combustion of rubber and of rubber-sulfur compounds. Measurements with a bomb calorimeter have been made of the heats of combustion of samples of rubber purified by various methods, and of compounds of rubber and sulfur containing up to 32 percent sulfur. The average value for the heat of combustion of ether-soluble rubber in gaseous oxygen to form gaseous carbon dioxide and liquid water at a temperature of 30° C. and a constant pressure of 1 atmosphere is 45,207 international joules per gram. The values obtained for the heats of combustion of compounds of rubber and sulfur may be represented by the equation  $Q_c = 45200 - 37823m$ , where  $Q_c$  is the heat of combustion in joules and  $m$  is the mass of sulfur per gram of compound. From these data, and the data of Eckman and Rossini on the heat of combustion of sulfur, the heat of combination of rubber with rhombic sulfur has been calculated to be 1,881 international joules per gram of sulfur and is independent of the percent of sulfur in the compound.

Gehman<sup>9</sup> studied the Raman spectrum of a solution of rubber in carbon bisulfide and carbon tetrachloride. Concentrations of rubber from 10 to 40 percent by volume were used. Raman lines were exhibited by a 4358A mercury line. Three most intense Raman frequencies for rubber are 1672, 1460, and 1382  $\text{cm}^{-1}$ . The Raman spectrum data appear to confirm the generally accepted views regarding the chain structure of rubber, although a cyclic structure is not definitely excluded, since cyclic terpenes have a spectrum of this nature.

Midgley and co-workers<sup>10</sup> have shown that natural rubber contains oxygen, while synthetic rubber is oxygen-free. The oxygen appears to be of an hydroxylic type, and its quantity corresponds to about one hydroxyl group for each 1,000 isoprene units of the rubber molecule. A mechanism of reaction has been proposed to interpret the quantitative data obtained.

Bridgman<sup>11</sup> applied a pressure of 50,000 kg/cm<sup>2</sup> to a specimen of crude rubber. The sample became a hard, translucent material, not unlike horn in appearance. The change was permanent. Sackett<sup>12</sup> studied the deleterious effect of manganese salts in plantation rubber. He studied also the consumer's crude rubber requirements.<sup>13</sup> Ingman-son and Mueller<sup>14</sup> developed a process of treating gutta percha which comprises cold leaching of the resins from the gutta hydrocarbon by petroleum naphtha, heating to 100° C. to expel the naphtha, and allowing albane to precipitate out at room temperature.

**Plasticizers.** One of the first production operations in the manufacture of a rubber article is the milling of the crude rubber. The mill rooms are large consumers of power and labor. Testing machines have been devised to measure the plasticity of milled rubber and are used to maintain uniformity. Technologists have been attempting for years to discover plasticizers which will lessen the time of milling without affecting the workability of green stock and the quality of the finished product.

Williams and Smith<sup>15</sup> have investigated the use of hydrazine and its derivatives as rubber plasticizers. They advance the theory that hydrazine may react chemically to assist in the destruction of a carbon-carbon bond in the rubber molecule, it may react chemically without the rupture of a carbon bond in such a manner that the attraction between molecules of rubber is decreased, or it may act in a purely physical manner to decrease the intermolecular forces in the rubber.

Tuley<sup>16</sup> claims a method for breaking down crude rubber by adding an oxide of lead and then milling at a temperature sufficient to reduce its viscosity. He also proposes the breaking down of crude rubber prior to compounding by adding a relatively stable aryl peroxide in an amount sufficient to reduce the viscosity of the rubber.<sup>17</sup>

Gibbons<sup>18</sup> has devised a means of improving physical properties of rubber by plasticizing a body of solid rubber by adding, at the beginning of its breakdown, a substance which furnishes upon hydrolysis a sufficient concentration of hydrogen ions to decompose the alkali proteinates and alkali soaps.

King and King<sup>19</sup> have developed a thermo-plasticizing composition made of a hydrocarbon solvent, non-volatile at vulcanizing temperature, and an oil-soluble sulfonated product as activator. This composition acts on unmasticated rubber to enable it to be readily plasticized. They<sup>20</sup> also claim that, by the addition of a small amount of non-liquid softener, unworked raw rubber becomes more readily plasticized and is made ready for compounding without preliminary mastication and with a saving in time and power required. Hyman<sup>21</sup> claims as a rubber plasticizer the high pressure liquid phase polymerization product obtained from cracking gasoline at 450 to 750° F.

**Vulcanization and Structure of Vulcanized Rubber.** Thibodeau and McPherson<sup>22</sup> have studied the photoelastic properties of soft, vul-

canized rubber. A study was made of double-refraction under tensile stress of transparent, vulcanized rubber at about 25° C. by means of a Babinet compensator, using light of wave length, 5461 Å. The relative retardation per unit thickness and the stress-optical coefficient were found to be related to the stress by equations of the form  $D_m = aT + bT^2 + cT^3$ , and  $C = a + bT + cT^2$ , where  $D_m$  is the retardation coefficient,  $C$  the stress-optical coefficient,  $T$  the stress, and  $a$ ,  $b$ , and  $c$  are constants for any given rubber compound. Formulas for the compounds investigated, in parts by weight, were given. The parameters  $a$ ,  $b$ , and  $c$  were functions of the type of compound. The values of  $a$ ,  $b$ , and  $c$  were given under the different conditions.

Nutting, Squires, and Smith<sup>23</sup> discuss the effect of cure on some physical properties of a high-sulfur rubber mix. A mixture of smoked sheet 100 and sulfur 50 was vulcanized isothermally through the range from soft rubber to ebonite, and the sulfur coefficients of vulcanization, tensile strengths, ultimate elongations, and densities were determined as vulcanization progressed. A table and graphs show these properties as functions of the time of vulcanization.

Smith and Holt<sup>24</sup> have studied the vulcanization and stress-strain behavior of sol, gel, and total rubber hydrocarbon. The stress-strain properties in three different types of vulcanization were found to be similar for each type of cure. Vulcanized rubbers prepared from the insoluble rubber hydrocarbons were less extensible, and those prepared from the soluble rubber hydrocarbon more extensible, than those prepared from the total rubber hydrocarbon.

Garvey,<sup>25</sup> as the result of experiments, concludes that the main vulcanizing effect of sulfur chloride is a catalytic reaction rather than an addition to the hydrocarbon.

Williams<sup>26</sup> concludes that vulcanization appears to consist of a chemical reaction that is accompanied by changes of a colloidal nature. The experiments which were described lead to the conclusion that vulcanization is the result of several actions which take place to a varying extent under different conditions.

Somerville<sup>27</sup> vulcanizes rubber by introducing a catalytic anti-oxidant to prevent oxidation by atmospheric oxidation to which the compound may be exposed, an organic oxygen absorber to eliminate any oxygen initially present in the compound, and an organic base to activate the organic absorber.

**Accelerators.** Since the discovery of the use of organic accelerators in the vulcanization of rubber by George Oenslager in 1906, this field of investigation has been explored by many chemists. Each year the patent literature discloses new and more complicated organic compounds.

*Aldehyde Amines.* Cadwell<sup>28</sup> claims that the products obtained from treating a preformed heptaldehyde and an aniline condensation product with a strong mineral acid gave a new class of compounds suitable for the vulcanization of rubber. Powers<sup>29</sup> produced a high

boiling viscous liquid or resinous solid accelerator by the reaction of an aldehyde, a primary aromatic amine, and carbon disulfide with the elimination of water. Sebrell<sup>30</sup> used the product resulting from the reaction of acetaldol with aniline and the further reaction of this material with formaldehyde. Messer<sup>31</sup> investigated the reaction product of formaldehyde, a 2-mercapto-aryl-thiazole of the benzene series, and a primary aromatic amine of the benzene and naphthalene series.

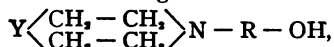
*Mercaptobenzothiazole.* Sebrell and Clifford<sup>32</sup> claim di-(aryl-thiazyl) monosulfide and an accelerating amine. Sebrell vulcanizes rubber in the presence of a mercaptothiazole in combination with a compound selected from the group consisting of ammonia, amines having a primary amine group, aliphatic amines, and alkyl aryl secondary amines.<sup>33</sup> Sebrell<sup>34</sup> has also patented a method of preparing mercaptan-amine derivatives, and Teppema<sup>35</sup> evolved a process of preparing carbamyl disulfides. Teppema<sup>36</sup> also uses thiazyl compounds of the group consisting of the nitrophenyl nitrobenzothiazyl sulfides and the nitrophenyl halo-benzothiazyl sulfides.

Williams<sup>37</sup> vulcanizes with an accelerator of the type mercaptobenzothiazole, diphenylguanidine, tetramethylthiuram monosulfide, and butyraldehyde-aniline, and an activator consisting of the zinc, lead, mercury, or cadmium salt of propionic acid. Semon and Ford<sup>38</sup> have patented a process for the manufacture of mercapto aryl thiazoles, which comprises heating a mixture of mononuclear arylamine and carbon disulfide with an organic oxidizing agent. Coleman<sup>39</sup> suggests the use of *N*-nitrosoarylaminoethyl arylenethiazyl sulfide for the vulcanization of rubber. Coleman<sup>40</sup> also claims a chemical compound which is the product of reaction of a mercaptobenzothiazole, formaldehyde, and a primary aromatic amine. Harman<sup>41</sup> studied the vulcanization of rubber, using an accelerator comprising the reaction product of an organic base and a mercaptoarylthiazole in the presence of a primary amine acid phthalate. Tuley<sup>42</sup> vulcanizes with mercaptobenzothiazole and an amino derivative of carbamic acid, adapted to decompose at vulcanizing temperatures to yield ammonia and an aliphatic amine.

Evans<sup>43</sup> prepares an accelerator by reacting a furoyl halide and a mercaptoarylthiazole in an aqueous medium containing a small amount of an inert organic solvent. Dunbrook and Zimmerman<sup>44</sup> describe a new method of preparing 2-mercaptobenzothiazole in one step from *o*-nitrochlorobenzene.

*Thiuram.* Cramer<sup>45</sup> prepares thiuram disulfides by a method which comprises oxidizing the sodium salt of a cyclic dithiocarbamate with ammonium persulfate. Northam<sup>46</sup> claims an accelerator consisting of thiuram polysulfide derived from a secondary amine, and thiuram monosulfide derived also from a secondary amine. Semon<sup>47</sup> accelerates vulcanization by heating rubber in the presence of a tetraaryl substituted thiuram sulfide.

*Miscellaneous.* Christensen <sup>48</sup> discusses a method of vulcanizing rubber by heating with sulfur in the presence of an accelerator composed of the reaction product of acetic acid and the product formed by reacting methylenedipiperidine and carbon disulfide. Coleman <sup>49</sup> accelerates the vulcanization of rubber by use of a vulcanizing agent and zinc oxide with *p,p'*-diaminodiphenylmethane as the accelerator. Sibley <sup>50</sup> discusses a process for retarding the vulcanization of rubber, which comprises heating a mixture of rubber, sulfur, and an accelerator comprising the crotonaldehyde derivative of the reaction product of mercaptobenzothiazole and hexamethylenetetramine in the presence of 2,4-dinitrophenol as a retarder of the accelerating action. Reed <sup>51</sup> claims accelerators of the general formula



where R is an aromatic nucleus, Y is CH<sub>2</sub>, O, S or *N*-aryl.

Lubs and Williams <sup>52</sup> vulcanized rubber by adding, before vulcanization, the products obtained by hydrogenating carbazole until at least part of the hydrogenated carbazole is soluble in 10 percent acetic acid. Meuser and Leaper <sup>53</sup> reacted a ketone and an aromatic amine, containing only secondary amino groups, at 100° C., using a hydrogen halide as catalyst. Sibley <sup>54</sup> has patented a process of preparing diphenyl derivatives—the sulfuric acid derivatives of the reaction products of a monohydric alcohol and a nuclear hydroxy substituted diphenyl and their alkali metal and alkaline earth salts. Clifford <sup>55</sup> prepares dithiazyl disulfides by a process which comprises oxidizing a thiazyl mercaptan with hydrogen peroxide in the presence of an inorganic acid. Gracia <sup>56</sup> prepares dithiazyl disulfides by heating an aqueous alkaline solution of mercaptobenzothiazole and mixing therewith an aqueous solution of hydrogen peroxide and an amount of sulfuric acid sufficient to neutralize said alkaline solution of mercaptobenzothiazole.

**Age Resisters.** The first age resister appeared on the market in 1921. Since that date the study of age resisters has been a fruitful field of research. Each year new organic compounds are added to the already long list of materials that are used to prolong the life of rubber compounds.

Tener and Holt <sup>57</sup> have studied the effect of antioxidants on the natural and the accelerated aging of rubber. Five different types of vulcanizates, in each of which were incorporated five common antioxidants, were (1) kept in darkness at room temperature for 7-8 years; (2) exposed outdoors for 16-20 months; (3) heated in air at 70° C. for 32-42 hours; (4) heated in air at 90° C. for 4-7 days; and (5) heated in oxygen at 60° C. under 300 lbs. per sq. in. pressure for 18-33 hours. Changes in tensile strength are shown in graphs. Two numerical criteria are suggested for expressing the effectiveness of antioxidants, a "time" index (the increased time during which a vulcanizate will remain serviceable) and a "tensile" index to show the

improvement in the integrated tensile strength over a definite period of aging effected by the antioxidant. Sommerville<sup>58</sup> presented a very interesting paper on the effect of oxygen absorbers in rubber to prevent cracking. Pyrogallol-ethanolamine and pyrogallol-quinolethanolamine combinations were used. Semon<sup>59</sup> has patented the condensation product of an unsaturated aliphatic ketone with a primary aromatic amine; the reaction product of a ketone with not more than two oxygen atoms with (1) an aromatic amine containing both primary and secondary amino groups; (2) an aromatic amine derived from benzene or an alkyl or alkoxy substituted benzene and containing only one primary amino group. Semon<sup>60</sup> also claims the use of symmetrical diphenyl substituted naphthylenediamine as an antioxidant. He has devised a method for preserving rubber by adding, before vulcanization, a plastic mass resulting from the cooling of a solution of a diarylamine in a molten neutral wax;<sup>61</sup> he prepared antioxidant by condensing an aromatic mono-amine with a ketone to produce an intermediate amine, and further reacting the intermediate amine with an aromatic mono-amine at a temperature at least 50° C. higher than that at which the intermediate amine is produced.<sup>62</sup> Sloan<sup>63</sup> retarded deterioration of rubber by treating with a poly-aryl carbinol containing one or two amino groups. He has also patented an antioxidant of the formula  $A-R-X-R'-A'$ , where A and A' represent amino groups, X an aliphatic nucleus, and R and R' represent aromatic nuclei attached to different carbon atoms of X.<sup>64</sup> Craig<sup>65</sup> uses an antioxidant consisting of diarylamines having at least one aliphatic hydrocarbon group which contains at least two carbon atoms substituted in the aromatic nucleus. Clifford<sup>66</sup> preserves rubber by treating with an aryl naphthylamine having at least one hydroxyl group substituted on an aromatic nucleus. Sibley<sup>67</sup> preserves rubber with the reaction product of one mole of acetone-anil and one atomic weight of sulfur. He also claims the use of an age resister consisting of products of one of these reactions: (1) dihydroxydiphenylmethane and an amine; (2) 2,4-tetrahydroxydiphenylmethane and *o*-toluidine or  $\beta$ -naphthylamine; (3) 2,3-tetrahydroxydiphenylmethane and  $\alpha$ -naphthylamine.<sup>68</sup> Calcott and Douglass<sup>69</sup> claim the use of a mono-hydroxy-diaryl methane as an age resister. Wolfe<sup>70</sup> uses the addition product of a mono-hydroxydiphenyl and an amine of the group consisting of primary aliphatic mono- and diamines, primary aromatic monoamines of the benzene and naphthalene series, benzylamine, cyclohexylamine and hexamethylenetetramine. Scott<sup>71</sup> preserves rubber by treating it with a sulfur derivative of a diaryl amine, a phenyl radical of said diaryl amine containing a nuclear alkoxy substituent only. Howland<sup>72</sup> preserves rubber by the use of the reaction product of an alkali metal upon a ketone-aromatic amine condensation product.

**Control and Testing.** Havenhill and MacBride<sup>73</sup> have devised a new laboratory machine for evaluating "breakdown" characteristics of rubber compounds. The new apparatus measures the flexing force

and also indicates the time of initial failure before destruction. The specimen is rotated between off-center plates, and samples may be compared under constant load or constant deflection. Unexpectedly the flexing force increases, i. e., the rubber stiffens on continued flexing, which indicates a structural change. The effects of volume loading, type of pigment, and other changes of ingredients are shown. Tests showed excellent correlation with service results, both for tire and carcass mixtures.

Holt<sup>74</sup> describes a study of the compression cutting test, also referred to as the shear test, for rubber. The test consists of compressing a sample of rubber to failure between a flat plate or anvil and a cutting tool and recording the relation between the thickness of the sample and the load up to failure. Data are presented on (1) different tools used for the test; (2) conditions affecting the results; and (3) a comparison of the compression cutting tests with other common tests. Advantages and disadvantages of the compression cutting test are discussed. The conclusion is reached that it is a valuable supplement to, rather than a substitute for, the tensile test.

McPherson and Bekkedahl<sup>75</sup> have developed a simpler method for determining the heats of reaction of rubber-sulfur. The description of the calorimeter methods and results is given and a comparison with the results of previous investigations is made.

Barnett and Mathews<sup>76</sup> show that good correlation exists between pendulum tests on rubber compounded with various types of zinc oxide and flexing life as measured by the Firestone flexometer. The effect of particle size of zinc oxide on the results obtained in both tests has been investigated and the optimum size found to vary greatly with changes in pigment loading.

Rainier and Gerke<sup>77</sup> have devised a new laboratory test for calculating the resistance to fatigue cracking of tire tread stocks. Data are given which show that ozone cracking and fatigue cracking are additive, that the rate of growth of cracks is a function of the maximum strain, that endurance limits may exist, and that the addition of antioxidants decreases the rate of growth of cracks and raises the endurance limit.

Scott<sup>78</sup> has determined the specific volume, compressibility, and volume thermal expansivity of rubber-sulfur mixtures containing from 3 to 31 percent sulfur at 10-85° C. at pressures up to 800 bars (790 atmospheres). The effect of the pressure on the specific volume was a function of the sulfur content and the temperature. The apparatus and technique are described and illustrated in detail.

McPherson and Bekkedahl<sup>79</sup> have studied the heats of reaction of rubber with sulfur to form vulcanized compounds having empirical formulas lying between  $C_5H_8$  and  $C_5H_8S$ .

Scott<sup>80</sup> determined the effect of pressure on the dielectric constant, power factor, and conductivity of rubber-sulfur compounds. The effect of pressure on the three properties varied with the sulfur content.

Wiegand and Snyder<sup>81</sup> claim that the rubber pendulum furnishes



a convenient method of visualizing and, to some extent, measuring the thermodynamical implications of the Joule effect; the extent and consequences of fatigue; the conditions for and degree of reversibility; and the way in which these properties vary with the state of strain, with temperature, and with other conditions. Clark<sup>82</sup> described the progress in x-ray research with rubber.

Sager<sup>83</sup> determined the permeability to hydrogen of a number of synthetic film-forming materials spread on closely woven cotton fabric. Of the films studied, those in which the molecule is rich in hydroxyl groups show very low permeabilities to hydrogen.

Walton and Osterhof<sup>84</sup> encountered numerous difficulties in attempting to rate rubber carbon blacks by means of heat of wetting measurements.

Fisher and Schubert<sup>85</sup> analyzed four samples of hard rubber for carbon and hydrogen content. Sulfur apparently adds to the rubber hydrocarbon until saturation is complete before any substitution takes place, provided proper vulcanizing conditions are maintained. It is pointed out that the carbon-hydrogen ratio is one of the best indications of substitution by sulfur.

Kraemer and Lansing<sup>86</sup> have used the Svedberg ultracentrifuge to determine the molecular weights of ether-soluble sol rubbers and of polychloroprenes. The molecular weights as determined in the ultracentrifuge are several times as great as Staudinger's viscosity values.

Ward and Gehman<sup>87</sup> have determined the rubber content of latex optically in an extinction cell by the use of a green filter.

Cole<sup>88</sup> has studied the effect of binary mixtures of zinc oxide, channel black, and clay on the physical properties of rubber. Hardman and Barbehenn<sup>89</sup> report that the long-used method of fixing the free sulfur in the acetone extract of vulcanized rubber by means of copper gauze gives the true free sulfur in vulcanizates containing acetone-soluble organic sulfur compounds or other interfering substances.

De Vries<sup>90</sup> has shown that the density of latex is not a linear function of the percentage rubber by weight. Because of De Vries' work, Rhodes<sup>91</sup> has reexamined the data on the density of rubber in latex and has corrected the value from 0.902 to 0.9064.

Dillon and Torrance<sup>92</sup> used an extrusion plastometer in the pressure measurements exerted by rubber on the walls of the die of a tubing machine; the results obtained were employed in correlating the plastometer with a tubing machine.

Humphrey<sup>93</sup> has devised a new method of determining guanidine in uncured rubber stocks.

Abbott and Sloman<sup>94</sup> describe a traveling test track capable of movement and of being dusted for the testing of tires.

**Compounding Ingredients.** Schoenfeld<sup>95</sup> has investigated the surface chemistry of carbon black and its effect on the vulcanization of rubber. There are so many different theories to explain the retarding effect of channel carbon blacks on vulcanization that a systematic study

was carried out to ascertain to what extent (1) physical adsorption, where the adsorbed substances are recoverable, (2) activated adsorption, with probable formation of molecular complexes and only partial recovery, and (3) solution of the adsorbed substances by the carbon black are responsible for the retardation. Blacks treated in various ways to alter their adsorptive power showed no relation between their adsorptive power and their influence on the rate of vulcanization. Channel black heated with sulfur and extracted with acetone gave a sulfur-bearing black (2.61 percent sulfur), which was used in rubber mixtures compensated and not compensated for sulfur; the sulfur in such a black is inert, but it alters the surface properties and thus increases the rate of vulcanization. Study of the impurities in gas blacks by means of blacks treated in various ways and added to mixtures accelerated with basic and acidic accelerators showed, among other inert components, an acid molecular complex of carbon and oxygen which is removable only at very high temperatures, and which retards the rate of vulcanization in a way similar to organic acid retarders. Extraction of black with concentrated ammonia, evaporation *in vacuo*, washing with ethyl alcohol, and evaporation *in vacuo* gave a mixture of unidentified organic acids, one of which behaved like mellitic acid. These acid components are the determinant factor in the retarding effect of blacks on vulcanization.

Park and Morris<sup>96</sup> have studied the effect of stearic acid and other so-called dispersing agents on the dispersion of channel gas black. Experiments show that channel gas black disperses with difficulty in rubber in which the acetone-soluble components are reduced to 0.5 percent or less. The addition of stearic acid to such extracted rubber facilitates the dispersion, which is a direct proof that stearic acid is a dispersing agent for gas black in rubber. Because of these facts, acetone-extracted rubber may be used as the basis of a method for testing the effect of various agents on the dispersion of gas black in rubber. In this way, various substances were found to improve the dispersion of gas black, others were without influence, and still others were antagonistic to the dispersion. The dispersing power of a given agent for gas black in rubber bears no relation to the deflocculating action of the agent on the same black in a paste with dipentene.

Wiegand<sup>97</sup> has shown that glycerine improves the curing behavior of tread mixings accelerated with mercapto and softened with pine tar. The effect of direct addition of glycerine, without reduction of tar, was quite marked, whereas similar direct addition of higher aliphatic alcohols was without specific effect. A pre-cooked mixture of one part glycerine with three parts of medium pine tar improved the rate of cure, modulus, and tensile strength of a mercapto tread stock containing 50 percent of carbon black, as compared with a control using straight pine tar. The above conclusions, since they do not include aging results nor road tests for abrasion resistance, must be accepted

as preliminary, but seem to warrant a further study of glycerine in tread compounding.

Smith<sup>98</sup> presents a historical review of the uses of coal tar products in rubber. He describes the use of cumar as a rubber ingredient. Jack<sup>99</sup> discusses the use of wood flour as a compounding agent in rubber.

Spear<sup>100</sup> claims the production of a carbon black by the thermal decomposition of a mixture of a hydrocarbon gas with twice its volume of diluent gas, followed by passing the mixture over high temperature surfaces. The solid carbon particles are separated from gaseous decomposition products. Spear<sup>101</sup> also claims a carbon black identified by the following physical characteristics (1) apparent density 0.37; and (2) maximum loading value in rubber when compounded therein as a reinforcing agent in excess of 100 but not substantially in excess of 150.

Wiegand<sup>102</sup> claims a process for the manufacture of carbon black, which consists of burning a hydrocarbon gas in a restricted supply of oxygen, causing the flame to impinge upon a cooler collecting surface, and subjecting the deposited carbon black to controlled oxidation by an oxidizing atmosphere between 300 and 1000° C. to produce a carbon black of improved color and workability. Wiegand<sup>103</sup> also claims a carbon black of high color intensity and a high degree of workability.

Richardson<sup>104</sup> has developed a process for producing hydrogen and carbon black, which consists of mixing hydrocarbon gas and steam and heating to effect thermal decomposition. The relative amounts of carbon black to gases are controlled by relative volumes of steam and hydrocarbon.

Odell<sup>105</sup> claims a fine particle size carbon black formed by thermal decomposition of a gas, which consists of pure carbon nuclei with the vapor of a metallic catalyst on the surface.

Park<sup>106</sup> has patented a pigment comprising a dried froth formed by co-precipitating a mixture of barium sulfate and ferric oxide, using pine tar, pine oil, cresylic acid, *m*-, *o*-, or *p*-cresol as foaming agent. Coolidge and Holt<sup>107</sup> claim that a pigment is rendered non-caking by the addition of from 0.25 to 1.0 percent of a protective agent dispersed in a liquid medium, said agent being taken from the group consisting of rubber, rubber latex, balata, and gutta percha, whereby a film is deposited on individual pigment particles when the mass is dried.

Gray and Kemp<sup>108</sup> have patented a vulcanizable insulating compound for coating electrical conductors at 160° F. and 400 feet per minute. The compound contains rubber, plasticizer, softener, and ultra accelerator.

Cowdery<sup>109</sup> has advanced a composition comprising rubber compounded with coal tar free from crystalline material. Cowdery<sup>110</sup> also claims the use of an oil resin containing one to five parts of heat polymerized cumarone resin and five parts of coal tar oil boiling at 170° C. as a compounding ingredient. Bergeim<sup>111</sup> proposes the use of a com-

position comprising rubber and a coal tar distillate, the distillate boiling above 200° C. under atmospheric pressure. Frolich<sup>112</sup> uses a rubber composition containing an asphaltene powder derived from cracked petroleum tar, free from hydrocarbon oils and resins.

Minor<sup>113</sup> proposes the addition of triethanolamine which has absorbed an equal volume of carbon dioxide gas to a rubber compound as an agent for the preparation of sponge rubber.

Kiernan<sup>114</sup> uses a leuco compound of a vat dye, which has been prepared by the action of a reducing carbohydrate, to color unvulcanized rubber. Croakman<sup>115</sup> uses the leuco compound of a dye with latex, followed by oxidation, to obtain a colored, vulcanized rubber. He also mixes the leuco compound of a dye with solid, unvulcanized rubber, followed by oxidation, to obtain a colored, vulcanized product.<sup>116</sup>

Damon<sup>117</sup> claims to have improved carbon black, intensifying the color by continuously agitating a charge and subjecting it to a slow oxidation at a temperature below that at which calcining takes place but high enough to increase the stable oxygen content of the carbon black. Bolton and Hayden<sup>118</sup> have developed a process for preparing a rubber composition containing carbon black and an open chain aliphatic alcohol of at least eight carbon atoms.

**Rubber Technology.** Davies<sup>119</sup> discusses the discoloration and transparency in vulcanized rubber. Discolorization originates from various causes, including natural components of the latex, putrefaction of protein, contamination with iron, smoke and dust, the natural brown color of the rubber-sulfur compound, and impurities in nominally colorless or white compounding ingredients. This discoloration makes the production of colorless transparent vulcanized rubber and white vulcanized rubber impossible without excessive loading.

Keenan<sup>120</sup> gives a short discussion of the uses of aluminum in the rubber industry. It is used for molds because it heats evenly, requires little cleaning, is immune from attack by sulfur, sulfur compounds, rubber solvents, and ammonia, is strong, hard, light, cheap, and inert, and gives a very smooth surface, dimensional accuracy, and good detail.

Peterson<sup>121</sup> discusses new uses of rubber. He mentions the use of sponge rubber as an expansion joint for highways. The rubber lasts 15 to 20 years. Townsend<sup>122</sup> discusses the application of latex in the preparation of paper fibers. Madge<sup>123</sup> makes rubber thread by forcing an aqueous dispersion of rubber through a nozzle into a coagulant, the nozzle being cool enough to freeze the dispersion. Minor<sup>124</sup> manufactures sponge rubber by adding an inert gas under pressure to the latex and vulcanizing, the water escaping as steam, which condenses.

Gilbert and Malm<sup>125</sup> impregnated a cable conductor with material formed from a composition of matter comprising at least semi-fluid depolymerized natural rubber mixed with an antioxidant not soluble in water.

Muller<sup>126</sup> proposes a degummed or artificial silk fiber treated with

a solution of the reaction product of rubber with chlorostannic acid. Bodle<sup>127</sup> makes a decorated rubber article by electrodeposition of the rubber in the cavities of an engraved anode plate, transferring the deposited rubber to an unvulcanized rubber surface by adhesive contact therewith, and vulcanizing.

Hoover<sup>128</sup> explains how the excessive wastes in the pickling of steel may be eliminated by the use of a new type of rubber-lined acid tank.

**Cements and Adhesives.** Contributions to cements and adhesives have appeared in the patent literature from the laboratories of the consumer industries.

Kronquest and Robison<sup>129</sup> have patented a coating dough for producing a coating material, comprising a mixture of 100 parts of rubber solution containing 30 parts rubber, 15 parts adhesive ester gum, 3 parts liquid petrolatum, and approximately 100 parts of zinc oxide.

Williams and Smith<sup>130</sup> reduce the viscosity of rubber solutions by the addition of a small amount of unsymmetrical substituted hydrazine.

Kronquest and Robison<sup>131</sup> have patented a liquid coating material for sealing the seams of cans—a mixture of rubber, zinc oxide, an adhesive ester gum, a plasticizer, sulfur, an accelerator, an antioxidant in a volatile solvent for the rubber and the gum. Kronquest and Robison<sup>132</sup> have also patented a coating material of milled rubber (30 parts rubber and 80 parts zinc oxide), an adhesive gum, and a plasticizer.

Robinson<sup>133</sup> claims a composition for lining can ends which consists of a solid body material, a solution of latex, and fortified ammonium alginate. Bollman and Ornes<sup>134</sup> claim a liquid adhesive adapted to vulcanize firmly and secure durably a plastic rubber composition to leather-like surfaces.

**Reclaiming.** Reclaimed rubber has played an important rôle in stabilizing the price of crude rubber. The principle use of reclaim rubber is in mechanical goods. As the price of crude rubber advances, the use of reclaim will increase, and more attention will probably be devoted to research in this important field.

Lane<sup>135</sup> reclaims rubber by heating fiber-containing vulcanized scrap with a small amount of caustic alkali. Busenburg<sup>136</sup> claims a method which comprises shredding scrap rubberized fibrous material, removing the major portion of the rubber from the shredded material, partially decomposing the remaining shredded essentially fibrous material by treatment for at least eight hours with steam at superatmospheric pressure, and physically disintegrating the treated material to produce a relatively free flowing earth-like product.

Campbell<sup>137</sup> has devulcanized scrap rubber by introducing an oil, including benzene, toluene, xylene, and a heavy solvent, into a digester with a desulfurizing agent. Upon application of heat and pressure in the presence of moisture, the rubber swells and softens, thereby allowing the desulfurizing agent to react.

Fairley<sup>138</sup> has patented a process of treating vulcanized rubber which

comprises subjecting vulcanized rubber to destructive distillation up to 400° C., continuing the distillation until a dry residue is obtained, condensing all resultant vapors, and collecting the mixture of vapors as a single distillate. Davies<sup>139</sup> has patented a method of treating rubber to produce depolymerization which comprises subjecting the rubber to the action of caustic soda and a hypochlorite.

**Hard Rubber.** Kemp and Malm<sup>140</sup> give a resumé of the literature on hard rubber, including vulcanization, chemical and physical properties, compounding, and mechanical and electrical properties.

Edland<sup>141</sup> makes hard rubber products by vulcanizing rubber mixtures with a percentage of sulfur sufficient to form hard rubber and with the addition of a sufficient amount of selenium to accelerate the vulcanization but not exceeding about 14 percent of the sulfur.

**Latex and Rubber Dispersions.** Latex and rubber dispersions are playing an increasingly important rôle in the rubber industry. A book "Latex in Industry" has been written by R. J. Noble and published by "Rubber Age."

Cotton<sup>142</sup> gave a review and discussion dealing with latex as a colloid system, surface phenomena, stabilization, coagulation, concentration, compounding, filler dispersions, viscosity, surface tensions, the influence of humidity, "setting," heat sensitizing, drying ornamental surfaces, and vulcanization. McGavack<sup>143</sup> discussed the use of latex as wire insulation and described latex purification, water absorption, advantages of latex insulation, and the electrical properties of the product.

McGavack and Tefft<sup>144</sup> have prepared a water-resistant rubber for electrical insulation, containing creamed latex with wax dispersed in it and an ammonium soap of the wax. Tefft<sup>145</sup> uses a latex containing up to 0.5 parts of a water-soluble alkylated cellulose per 100 parts of latex solids for creaming. McGavack<sup>146</sup> patented a process for increasing the rate of creaming of latex by subjecting a mixture of creaming agent and latex to a violent shearing stress for a brief period of time, then allowing the serum and rubber-rich portions to separate by gravity. McGavack<sup>147</sup> also thickens latex with a small amount of hydrophilic colloid, introducing additional amounts of said hydrophilic colloid into at least a portion of the serum, and mixing the thus-treated serum with the cream portion.

Madge<sup>148</sup> claims a golf ball thread deposited directly from latex, having smooth faces and rounded edges.

Noble<sup>149</sup> claims a process which comprises adding to rubber latex a water-soluble stabilizer, flocculating the latex with a chemical that insolubilizes the stabilizer, dewatering the rubber flocs partially, then adding water and a chemical that restore the insolubilized stabilizer, thereby causing the mass to revert to latex. Noble<sup>150</sup> has also prepared granulated rubber from rubber latex by adding an insolubilizable hydrophilic stabilizer to the latex, flocculating the latex with an agent

that insolubilizes the stabilizer, separating the flocs, dewatering and granulating the cake.

Leguillon<sup>151</sup> makes a decorated rubber article by using two distinct types of plastics, a body stock, and a surface-decorating stock. The body stock is roughly formed to desired pattern and then the decorating stock with a lower plasticity is poured on and the whole vulcanized in a mold under pressure. Leguillon<sup>152</sup> also decorates rubber articles by applying to a body of rubber a multitude of bodies of decorating stocks of at least two different light reflectivities. This forms a surface with a multitude of diffusion planes. Leguillon<sup>153</sup> makes multicolored rubber articles by producing a localized deposit of rubber in the cavities of an open cavity engraved mold.

Szegvari<sup>154</sup> makes rubber articles by a method which comprises applying to a base surface a coagulant whose thickness varies over the surface and thereafter applying a coagulable dispersion of rubber and drying the coagulated rubber.

Linscott<sup>155</sup> has patented a stable concentrated latex composition capable of producing a dried rubber film substantially free of water-soluble ingredients, comprising a creamed latex containing a soap of a voltatile base and a soap forming acid, and a volatile resin solvent which is a non-solvent of rubber.

Williams and Dales<sup>156</sup> stabilize artificial and natural latex by adding sulfonated abietane or sulfonated abietene and sulfonated abietine.

Hazell<sup>157</sup> manufactures a rubber fabric by applying a coating of rubber from an aqueous dispersion to a fabric and applying another coating of rubber which is less basic (alkaline) than the first. Winchester<sup>158</sup> prepares rubber goods directly from latex by applying a dehydrating agent to a form, alternately dipping the form in a bath of latex and removing it to the air, and drying the whole when the desired thickness is reached. Dehydrating agents used are bentonite, wilkenite, and ardmorite.

Partridge<sup>159</sup> prepares an artificial rubber dispersion by dispersing the aqueous medium in the rubber and then inverting the phases of the dispersion by adding a soluble peptizing agent capable of furnishing polyvalent negative ions. Levin<sup>160</sup> produces a cellulose-rubber mixture by mixing a solution of viscose with an aqueous suspension of rubber, adding a chloride of an alkaline earth metal, heating, and recovering the solid components.

Willson<sup>161</sup> claims a coagulant composition, comprising a latex coagulant, a volatile organic solvent, and a substance which improves wetting of the form and also of the residue. Cake<sup>162</sup> preserves latex with a mixture of phenol, soap, ammonia, and alkali metal hydroxide.

Chapman and associates<sup>163</sup> control the speed and degree of thickening of a latex dispersion by addition of a salt of hydrofluosilicic acid.

Messer<sup>164</sup> claims a latex composition containing a vulcanizing agent and a water-soluble dithiocarbamate. Erdahl<sup>165</sup> uses a composition of matter comprising alginic acid and rubber latex. Grupe and Kienle<sup>166</sup>

claim a plastic composition comprising a mixture of vulcanized rubber or rubber latex and an alkyl resin.

**Synthetic Rubber and Rubber-Like Products.** Brous and Semon<sup>167</sup> present some of the properties and uses of a new plastic, "Koroseal." The generic term "Koroseal" refers to a particular class of compositions with properties varying from those of hard rubber to those of a jellied rubber cement embodying modified, substantially insoluble polymers of vinyl halides. By a suitable choice of raw materials in proper proportions and of methods of processing, a variety of useful rubber-like products can be prepared, the chemical and physical properties of which depend upon the above factors. The processing, compounding, physical and chemical properties, and applications are discussed. Koroseal is characterized by remarkable resistance to various oils, mineral acids, alkalies, oxygen, and radiation.

Korolac is the solution of Koroseal and is recommended for covering plating-racks.<sup>168</sup> It withstands alkalies, sulfuric acid, nitric acid, hydrochloric acid, hydrofluoric acid, chromic acid, and water. Its film is tough and elastic and easily repaired. Korogel is the jelly form of Koroseal and is used for molds for plaster of Paris, Keene's cement, Portland cement, Hydrocal, and other types of synthetic stone. It gives fine detail and will not dry out. It can be remelted and re-used.

Special mention is given to a type of coating with a trade name of Thiokol C-103.<sup>169</sup> It can be sprayed, spread, dipped, or brushed on. It bonds solidly to most surfaces, and it does not age. It is highly resistant to aromatic hydrocarbons and chlorinated solvents.

Thiokol D is an oil-proof synthetic rubber with a tensile strength up to 1,700 lbs. per square inch.<sup>170</sup> It is flexible at  $-45^{\circ}$  F. and resistant to hot oil at  $200^{\circ}$  F.

Reed<sup>171</sup> claims as a plastic composition and process of making the same a homogeneous and amorphous composition, comprising rubber together with a vinyl resin identical with a resin resulting from the conjoint polymerization of two different vinyl esters.

Brooks<sup>172</sup> has patented a process of making a rubber-like material by separating mono- and diolefins of four to five carbon atoms from a mixture of hydrocarbons. The diolefins are separated from the mono by cuprous chloride and the former polymerized to form a rubber-like material.

Nieuwland<sup>173</sup> presented a general paper on the preparation, properties, and uses of DuPrene.

Carothers and Berchet<sup>174</sup> claim a process which comprises reacting 1,2,3,4-tetrachlorobutane with an alkaline compound which will remove hydrogen chloride from the said chlorobutane.

Collins<sup>175</sup> uses an aqueous dispersion of a halogen-2-butadiene-1,3 and protein in which the ratio of one to the other is never greater than 9:1.

Gibbons and Smith<sup>176</sup> produce a styrol from alkyl benzol by pyrogenically dehydrogenating material containing sulfur, whereby the



released hydrogen combines at least in part with the sulfur, and separating the styrol from the reaction by-products.

**Derivatives of Rubber.** Calvert<sup>177</sup> has patented a transparent film composed of a rubber hydrohalide and a substance to retard photochemical disintegration of the rubber hydrohalide.

Baymiller<sup>178</sup> proposes the treatment of a rubber surface by subjecting it to the action of a solvent for a sufficient time to cause slight flowing of the surface and then to the action of a halide of an amphoteric element.

Ford<sup>179</sup> prepares a derivative of rubber by heating a mixture of rubber, a smaller proportion of an aldehyde, and a phenol in the presence of an aromatic sulfonic acid. McGavack<sup>180</sup> has produced chlorinated rubber by introducing chlorine into the vulcanized latex.

**Miscellaneous.** Thies<sup>181</sup> proposes the use of a small amount of furoic acid to prevent the scorching of rubber.

Fine<sup>182</sup> has shown that the use of rubber cements as a constituent of paints is made possible only by the reduction of viscosity. A number of catalysts have been tried and formulas developed that yield ready-mixed paints, as well as gloss paints with improved qualities. At present the addition of rubber to enamels has not been as satisfactory as in the case of paints.

Jacobs<sup>183</sup> has patented a paint consisting of a liquid composition comprising crude rubber, solvent naphtha, petroleum, turpentine, linseed oil, China wood oil, kauri gum, ester gum, manganese borate, zinc sulfate, and red lead in such proportions as to make the composition suitable for use as a paint.

Fairley<sup>184</sup> prepared a varnish gum by a method which comprises subjecting vulcanized rubber to destructive distillation until a dry residue is obtained, collecting the mixture of vapors as a single distillate, heating said distillate in contact with nitric acid, and cooling the reaction product. Fairley<sup>185</sup> also claims a flowable coating comprising a drying oil, which is the total distillate obtained by distilling vulcanized rubber to dryness, a resin, and a drier.

Holm<sup>186</sup> has patented an artificial leather from a mixture of rubber, fiber, and leather.

Werder<sup>187</sup> has patented a lubricant consisting of a heavy lubricant, a volatile solvent, and a rubber cement.

Weller<sup>188</sup> vulcanized rubber by interposing between the contacting surfaces of the article and the mold the salt of a polybasic acid ester of an alcohol having from 6 to 20 carbon atoms.

Seaman<sup>189</sup> developed a rubber solvent consisting of a liquid organic sulfide selected from the class consisting of alkyl thioethers and polysulfides.

Bonney and Egge<sup>190</sup> claim a protective coating composition consisting of a homogeneous mixture of chlorinated rubber and that component of oxidized drying oil which is separated from the unoxidized

and non-hardening constituents and is capable of hardening without further oxidation.

Lawson<sup>191</sup> isomerizes rubber with anhydrous fluoric acid.

Flint<sup>192</sup> claims a composition of matter comprising peracylated rubber and a film forming material of the class consisting of cellulose derivatives and resins, the peracyl group of said peracylated rubber being derived from a non-basic acid.

Rodman<sup>193</sup> claims a rubber composition containing a pigment and a dispersing agent selected from the group consisting of aliphatic dihydric and aliphatic trihydric alcohols containing at least eight carbon atoms.

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## Chapter XXIV.

### Unit Processes in Organic Synthesis.\*

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**Nitration.** Practically all of the recent contributions to the literature of nitration are concerned with the technical art and relate to some modification or slight improvement in industrial processes. As is to be expected, mixed acid (i. e., nitric-sulfuric acid) was the principal nitrating agent employed.

*Mixed Acid as a Nitrating Agent.* In the preparation of the isomeric nitrochlorobenzenes, an eutectic mixture (65 percent para and 35 percent ortho) is obtained after the *p*-isomer is crystallized out. When this mixture is submitted to dinitration with mixed acid (67 percent  $\text{H}_2\text{SO}_4$ , 33 percent  $\text{HNO}_3$ ) at  $60^\circ \text{C}$ ., the *o*-isomer is preferentially nitrated to 2,4-dinitrochlorobenzene, whereas, the *p*-isomer is largely unattacked.<sup>1</sup> Beard and Lulek<sup>2</sup> report the nitration of anthraquinone-2-carboxylic acid dissolved in about 100 parts of concentrated sulfuric acid with mixed acid; the same product can also be obtained by a similar treatment of the keto acid before cyclization.<sup>3</sup>

In the preparation of 4-nitro-2-aminotoluene<sup>4</sup> and 4-nitro-2-aminoanisole<sup>5</sup> from the corresponding amines, it has been found advantageous to treat the diluted reaction mass with naphthalene-sulfonic acids. A sulfonic acid salt of the amine is formed and precipitated. The free bases are obtained by washing and hydrolyzing the sulfonates. Another method of separating nitroamines has been proposed by Flett.<sup>6</sup> In the nitration of acetanilide, the *o*-isomer is separated by diluting the reaction mass to a residual  $\text{H}_2\text{SO}_4$  acidity of 65 percent and permitting the sulfate of the *p*-isomer to separate as crystals. The use of adsorbent silicious material, such as kieselguhr, to facilitate the separation of nitrobenzene from the spent acid is reported by Simon.<sup>7</sup>

Acetyl and benzoyl derivatives of 4,5,6-tribromoguaicol were nitrated with fuming nitric acid at room temperature.<sup>8</sup> The products were 2-methoxy-3-nitro-4,5,6-tribromophenyl acetate and

\* Compiled by the following authors of "Unit Processes in Organic Synthesis," McGraw-Hill Book Company, 1935: M. R. Fenske, P. H. Groggins, S. J. Lloyd, L. F. Marek, H. P. Newton, A. J. Norton, E. E. Reid, A. F. Shepard, R. N. Shreve, W. A. Simpson, A. J. Stirton, and H. E. Woodward.

2-methoxy-3-nitro-4,5,6-tribromophenyl *m*-nitrobenzoate, respectively. It is significant that no bromine was split off in these nitrations and that, in the last case, both nuclei were nitrated.

Craig<sup>9</sup> has studied the nitration of *tert*-butylbenzene with mixed acid, a mixture of 77 percent para and 23 percent ortho and no meta derivatives being obtained.

Michael and Carlson<sup>10</sup> have made an excellent study of the mechanism of the nitration process. With respect to the nitration of ethylene with mixed acid, they conclude the acid mixture must contain mixed anhydride,  $\text{HOSO}_2\text{ONO}_2$ , which should add readily to ethylene to yield  $\text{CH}_2(\text{OSO}_3\text{H})\text{CH}_2\text{NO}_2$ , from which the  $\text{SO}_3\text{H}$  group should be displaced by the more negative  $\text{NO}_2$  radical with the formation of pyrosulfuric acid and the nitro nitric ester. Groggins<sup>11</sup> has presented tabulated data indicating that nitration generally occurs through the intervention of simple or mixed anhydrides of nitric acid.

**Amination by Reduction.** During the past few years very little of real importance has been added to our knowledge of amination by reduction.

**Metal-Acid Reductions.** It was well known that, in the metal-acid reduction, the acid could be substituted by any salts which, in the presence of metals, are hydrolyzed in aqueous solutions, resulting in the formation of hydrogen ions. Calvert<sup>12</sup> has pointed out that a solution of ammonium chloride and finely divided iron can be used for the reduction of 2,4-dinitrodiphenylamine. It has also been shown that comminuted, tinned, ferrous scrap can be employed in reductions requiring iron.<sup>13</sup> Iron etched with hydrochloric or other suitable acids can be utilized for the reduction of nitro-biphenyl in benzene solution.<sup>14</sup> Zinc dust and a solution of zinc acetate and copper sulfate has been recommended for the reduction of nitroguanidine,<sup>15</sup> while zinc and HCl are suggested for the reduction of either *N*-(*p*-nitro- or nitrosophenyl)-morpholine.<sup>16</sup>

Sodium arsenite in alkaline solution is employed by Dahlen and Carr<sup>17</sup> for the preparation of 3,3'-diaminoazoxybenzene.

**Reduction by Hydrogenation.** Unsymmetrically substituted ethylenediamines<sup>18</sup> may be prepared by reducing nitriles (which are made by causing an aldehyde or ketone to react with a metal cyanide in the presence of a mineral acid) with hydrogen under pressure, and then causing the product to react with an amine. *p*-Nitro- or nitrosophenol in acetone can, likewise, be reduced by hydrogen in the presence of a platinum catalyst.<sup>19</sup> Wojcik and Adkins<sup>20</sup> have reported on an extensive investigation relating to the catalytic reduction of amides to amines. Machlis and Blanchard<sup>21</sup> have described the reduction of  $\alpha$ -isonitroso-4-propionylbiphenyl with hydrogen at 35 pounds pressure in the presence of palladiumized charcoal.

**Diazotization.** In recent years American chemists have shown a

moderate interest in the diazotization reaction, as shown by their publications.

Snow<sup>22</sup> has extended our knowledge of the effect of temperature and of substituting groups on the stability of diazonium compounds by quantitative studies on a series of 32 such compounds. He confirms the rule that negative groups increase the stability of diazonium compounds, and shows that many amines may be diazotised at higher temperatures than were formerly used. It has been known that 2-aminofuranes are not easily diazotised. Gilman and Wright<sup>23</sup> suggest that 3-aminofuranes are more easily diazotised because they are more basic. They describe the diazotization of 4-amino-5-acetyl-amino-2-furoic acid ethyl ester and some monoazo compounds obtained from it.

The diazonium group may be replaced by the acetate group, according to Haller and Schaeffer,<sup>24</sup> by reaction of diazonium borofluorides with acetic acid or acetic anhydride. Smith and Haller<sup>25</sup> report an exception to this reaction in the case of 1-amino-3,4-dimethoxybenzene, which gives 2-hydroxy-4,5-dimethoxyacetophenone, probably by rearrangement of the acetate first formed.

Clark<sup>26</sup> shows that 4,6-dinitrobenzene-2,1-diazo oxide is useful as a detonating agent for initiating the explosion of dynamite and other explosives. A method of obtaining this diazo compound in a free flowing form which makes its use practical is disclosed by Hancock and Pritchett;<sup>27</sup> the process consists of a gradual addition of acid to a solution of a picramate and a nitrite.

A process for obtaining a stable dry preparation which on addition to water gives a solution of a diazonium salt is reported by Kemmerich.<sup>28</sup> The preparation consists of the reaction of an amine, in the form of a condensation product with an aldehyde, with a nitrite and an acid salt, such as sodium bisulfate.

A peculiar reaction of diazotised aminopentamethylbenzene was observed by Smith and Paden.<sup>29</sup> With pentamethylbenzene, it reacted to give a colorless hydrocarbon,  $C_{22}H_{30}$ , not decamethylbiphenyl.

**Halogenation.** Reports and patents dealing with recent research and advances in the field of halogenation are so numerous that no detailed or adequate survey of the literature can be presented here.

**Chlorination (Hydrocarbons).** Sharp<sup>30</sup> describes the chlorination of propane with chlorine in presence of cupric or ferric chloride under the influence of actinic rays. The liquid phase monochlorination of pentane in the presence of polychlorinated products is also reported. Benzene in the liquid phase under 4 atmospheres pressure at  $-15^{\circ}$  C. gives a highly chlorinated product.<sup>32</sup>

**Acid and Alkyl Chlorides.** The conversion of carboxylic acids to acid chlorides is the subject of a number of patents. Thus, acid anhydrides may be treated with chlorine in the presence of phosphorus or phosphorus trichloride or alternatively phosphorus tri-

chloride in the presence of phosphorus oxychloride.<sup>33</sup> Phosphorus pentachloride in benzene solution is similarly employed for 1,4- or 1,5-anthraquinonedicarboxylic acids.<sup>34</sup> Conover<sup>35</sup> shows that benzoyl chloride may be obtained from phthalic anhydride by reacting with hydrogen chloride at 200° C. in the presence of a decarboxylating agent, such as chromium chloride.

The preparation of alkyl halides from alcohols and olefins has been the subject of widespread study. Daudt reports the preparation of alkyl halides by reacting ethanol with hydrogen chloride in the presence of bismuth chlorides.<sup>36</sup> The halogenation may also be carried out in the presence of zinc chloride.<sup>37</sup> Olefins may similarly be converted by hydrogen chloride in the presence of sulfuric acid or a metal halide catalyst, such as antimony or bismuth chloride.<sup>38</sup> *Tert*-butyl alcohol is converted to the alkyl halide by hydrogen chloride in the presence of calcium chloride,<sup>39</sup> while copper is employed to increase the yield of ethyl bromide from ethanol<sup>40</sup> when the reaction is carried out in aqueous sulfuric acid. The presence of copper results in the production of sulfur dioxide which reduces any bromine to bromide ion.

Lutz and Wilder<sup>41</sup> have studied the action of phosphorus pentachloride and thionyl chloride on 2,5-diphenylfurans and unsaturated 1,4-diketones. Phosphorus pentachloride reacts to produce 2,5-diphenylmono- and -dichlorofurans and also apparently adds to dibenzoylhydroxyethylene to give diphenyl-4-chloro-3-butene-1,2-dione. Thionyl chloride behaves similarly in some cases, but is not so active. 1-Aminoanthraquinone dissolved in nitrobenzene is chlorinated in the 4-position by the action of sulfuryl chloride<sup>42</sup> in the presence of aluminum chloride. Bass and Burlew<sup>43</sup> report the preparation of  $\alpha$ - and  $\beta$ -chloropropionic acids by chlorination of the acid with chlorine gas in the presence of the corresponding acid chloride.

**Bromination.** Raiford and Milbery<sup>44</sup> have brominated the benzoic esters of phenol and the cresols under different conditions and the position of the bromine was determined. Sachs and Peck<sup>45</sup> show that in the bromination of anthraquinone with bromine, chlorine under pressure can be employed to regenerate bromine *in situ* from the hydrogen bromide that is liberated.

**Fluorination.** Due to the economic value or potential possibilities of many fluorine compounds as refrigerants or in the manufacture of dyestuffs, research in this comparatively new field has been both intense and widespread.

With respect to the preparation of aromatic fluorine derivatives, Aelony<sup>46</sup> reports an improved method of synthesizing *m*-fluorobenzotrifluoride. The fluorination of hexachlorobenzene is discussed by Bigelow and Pearson.<sup>47</sup> The reaction of acyclic compounds with hydrogen fluoride and a hydrocarbon halide containing a halogen other than fluorine in the presence of ferric chloride



and activated carbon is recorded in one patent<sup>48</sup> and the use of antimony pentachloride and hydrogen fluoride in another.<sup>49</sup> Instead of antimony pentachloride, numerous other halides are suggested.<sup>50</sup>

For the preparation of aliphatic fluorine derivatives, e. g., dichlorodifluoromethane from carbon tetrachloride, Henne<sup>51</sup> suggests the use of antimony trifluoride and the addition of chlorine to the reaction zone. Henne and colleagues<sup>52, 53</sup> further elaborate on this process in subsequent patents, and the use of calcium fluoride<sup>54</sup> and antimony sulfate<sup>55</sup> are also reported. Daudt and his coworkers have also contributed largely to the advances in this field and their contributions are recorded in numerous patents.<sup>56-60</sup>

Calcott and Benning<sup>61</sup> describe the preparation of fluorochlorethanes by reacting tetrachloroethane with fluorine in an inert liquid medium.

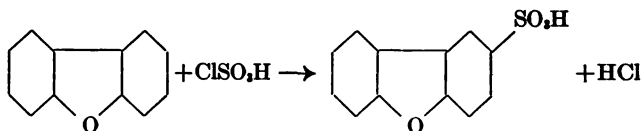
Deanesly<sup>62</sup> adds to our understanding of the halogenation process by his investigation of the inhibitory influence of oxygen in the chlorination of propane, butane, and pentane. In the addition of chlorine to olefins, no inhibition by oxygen was observed, but this may be due to the speed of the reaction.

**Sulfonation.** Recent contributions in the field of sulfonation indicate clearly a better understanding of the fundamental principles involved in this unit process. The use of cycle acids, the employment of sulfur trioxide in comparatively inert solvents, and the utilization of chlorosulfonic acid for the preferential sulfonation of one of two isomers exemplify the progress in the art.

In the sulfonation of benzene Carswell<sup>63</sup> employs a heel from a previous sulfonation and progressively adds definite proportions of oleum and hydrocarbon so that the sulfuric acid concentration in the sulfonator is at all times approximately 98 percent; sulfone formation is inhibited and the process may be carried out continuously.

Gubelmann and Rintelman<sup>64</sup> report an improvement in the production of the anthraquinone-2,6- and -2,7-disulfonic acids. The disodium salt of *p*'-sulfo benzoyl-2-benzoic acid is cyclized to form  $\beta$ -anthraquinonesulfonic acid by means of 1.5 parts of 25 percent oleum in the presence of a small amount of vanadium oxide. Disulfonation is then effected by adding two parts of 60 percent oleum and heating to 150° C. In this way a mixture of 2,6- and 2,7-anthraquinonedisulfonic acids is produced in a purer form than by the usual process starting with anthraquinone.  $\alpha$ -Isomers, oxidation products, and unreacted anthraquinone are largely avoided.

Chlorosulfonic acid was used by Gilman, Smith, and Oatfield<sup>65</sup> for sulfonating dibenzofuran in their study of the orientation of nuclear substituents. They found that sulfonation occurs in the 2-position and with great ease. An 89 percent yield was obtained.



Chlorosulfonic acid, in 5 percent excess, was dropped into a solution of the dibenzofuran in carbon tetrachloride at 25° C. This is the first time that orientation of a dibenzofuransulfonic acid has been definitely established.

An interesting and important use of chlorosulfonic acid is proposed by Kyrides.<sup>66</sup> The eutectic mixture obtained in the dichlorination of benzene is treated at 25° C. with chlorosulfonic acid, whereby the *o*-isomer reacts preferentially and the *p*-isomer is left unattacked.

The extended use of sulfur trioxide in inert solvents for direct sulfonations has progressed as was to be expected. Tinker<sup>67</sup> employs it in tetrachloroethane for the sulfonation of  $\beta$ -naphthylamine, while Weiland and Prahl<sup>68</sup> employ the same agents for the sulfonation of abietene. Temperatures of 0-25° C. are preferred.

The monosulfonation of biphenyl with concentrated sulfuric acid in the presence of nitrobenzene was disclosed by Stoesser and Marschner.<sup>69</sup> The reaction is not carried to completion, the unattacked biphenyl being separated. Biphenyl-4-sodium sulfonate is then obtained as colorless plates by treating the sulfonic acid with sodium sulfate.

Lauer and Langkammerer<sup>70</sup> investigated the action of sodium bisulfite solution on resorcinol at the boiling temperature and obtained the hitherto unreported sodium salt of phenol-*m*-sulfonic acid. The reaction mixture, after boiling, was treated with caustic soda and then hydrochloric acid. The sodium salt of phenol-*m*-sulfonic acid was then obtained from the evaporated and dried mixture by extraction with alcohol.

Reed and Tarter<sup>71</sup> studied the action of aqueous sodium sulfite on alkyl halides of higher molecular weights, by carrying out the reaction in an autoclave at about 200°. Bromides were used in their investigation, except in the preparation of sodium lauryl sulfonate, in which case lauryl chloride was used. Octyl, decyl, myristyl, cetyl, octadecyl, and lauryl sulfonates were prepared. This investigation settles a point of argument concerning the Strecker reaction and firmly establishes this reaction as a method of obtaining alkyl sulfonates of higher molecular weight.

Hitch and Black<sup>72</sup> describe a method of separation of 1-aminonaphthalene-5-sulfonic acid, "Laurent's Acid", from 1-aminonaphthalene-8-sulfonic acid, "Peri Acid". It is stated that the most effective means of separating these acids is to treat an alkaline solution of the two acids with sulfuric acid until the pH is adjusted to between 4.0 and 4.6. This treatment results in the precipitation

of the 1,8-acid, which is filtered off. The filtrate is then made acid to Congo, whereupon the 1,5-acid precipitates.

Adamson<sup>73</sup> studied the purification of 1-nitroanthraquinone-6-sulfonic acid from impurities present in large scale manufacture. This acid is an intermediate in the production of 1-nitro-6-chloroanthraquinone. It has been found that erratic results were obtained in the conversion of the sulfonic acid to the chloro compound unless the sulfonic acid was previously purified. It was found that the nitroanthraquinonesulfonic acid could be removed from impurities with practically complete success by recovering the sulfonic acid from a 40-45 percent sulfuric acid solution instead of the 70 percent residual acidity previously used. Sodium sulfate is used to decrease the solubility of the sulfonic acid.

**Amination by Ammonolysis.** The progress in this field has been characterized by improvements in the established art, rather than the introduction of new principles. Because certain groups of compounds require fairly specific treatment, this review is arranged accordingly.

*Aliphatic Halogen Compounds.* Lauter<sup>74</sup> has modified the process of Curme and Lommen<sup>75</sup> for the preparation of ethylenediamine from the corresponding dichloride. Instead of employing aqueous ammonia alone, a prodigious quantity of such salts, e. g., cuprous chloride, capable of forming a ternary addition complex with the reactant, is added. Upon hydrolysis of the complex, the diamine is obtained.

*Aromatic Halogen Compounds.* Wuertz<sup>76</sup> has extended the work of Groggins and Stirton<sup>77</sup> with respect to the use of ammonium salts and oxidants. Such compounds have been found useful in the preparation of amines which are not readily susceptible to oxidation. Such compounds inhibit the formation of hydroxy compounds and facilitate completion of the reaction.

*Treatment of Aliphatic Alcohols.* The vapor phase conversion of alcohols to amines has been the most active field of investigation. Arnold<sup>78</sup> thus prepares butylamine by passing the corresponding alcohol over a porous gel impregnated with a dehydrating oxide. Methylamine<sup>79</sup> is similarly prepared by passing the reactants over aluminum oxide<sup>80</sup> or activated charcoal.<sup>81</sup>

Bottoms<sup>82</sup> discovered that glycerol dichlorohydrin can be converted to 1,3 diamino-2-propanol by treatment with aqueous ammonia in the presence of sufficient alkali to form sodium chloride with the replaced chlorine. Isomeric isopropanolamines have been prepared by Wickert<sup>83</sup> by diffusing propylene oxide into aqueous ammonia.

*Treatment of Carbohydrates.* Flint and Salzberg<sup>84-86</sup> have developed procedures for the preparation of glucamines and related products by reacting glucose with aqueous ammonia or alkylamines in the

presence of a nickel catalyst and under a hydrogen pressure of 1500 pounds.

Calcott<sup>87</sup> has prepared secondary and tertiary amines by treating *N*-glucyl-*N*-methylamine with cetyl chloride at 150° C. in a copper autoclave. Bruson<sup>88</sup> has discovered that amides can be prepared from fatty acids by reacting in open vessels with urea at 180 to 250° C.

**Oxidation.** Considerable money and effort has been spent in attempts to make use of two basically cheap chemical raw materials, i. e., air and the aliphatic hydrocarbons of petroleum, for the formation of more valuable oxygen-containing compounds. An historical account of this work has been given by Marek and Hahn.<sup>89</sup> From the standpoint of the use of petroleum as a raw material for chemical synthesis, Ellis<sup>90</sup> has given an account of the work dealing with oxidation. Other reviews have appeared, many of them associated with original work.

Wiezevich and Frolich<sup>91</sup> have discussed their laboratory and semi-commercial work on the direct oxidation of saturated hydrocarbons at high pressures, the results of which showed the possibilities for the formation of oxygenated compounds from methane, ethane, propane, butanes, pentanes, and heptanes as raw materials. Elevated pressures were found to lower materially the temperatures necessary for reaction. An extensive bibliography is given.

The kinetics of oxidation has been studied further. Pease and Munro<sup>92</sup> report on the slow oxidation of propane, having investigated liquid as well as gaseous products. The reaction was found to be highly autoaccelerating, to be suppressed by inert foreign gases and by glass packing, and to have no simple kinetic scheme. Pease<sup>93</sup> also found that slow oxidation of propane at low temperatures and low oxygen concentrations gave rise to formation of methanol, formaldehyde, carbon monoxide, and water as the primary products.

Few details are available on the results obtained from oxidation of petroleum fractions. Sheely and King<sup>94</sup> show that vapor phase oxidation of kerosene leads to the production of a mixture of aldehydes and acids containing from 8 to 10 carbon atoms per mole. Burwell<sup>95</sup> also has discussed the formation of fatty acids from petroleum by low-temperature, liquid-phase oxidation, on the basis of several years of practical work.

Frear<sup>96</sup> studied the nature of methane-oxygen reaction by the flow method. Studies have been reported on the oxidation of 2-butene, in which the principle products were found to be acetaldehyde and butadiene, and less important products to be glyoxal, olefin oxide, acids, and some peroxide.<sup>97</sup> Oxidation of triisobutylene has been studied from the standpoint of evaluating the structure of the acids obtained.<sup>98, 99</sup>

Oxidizing agents other than oxygen itself form a large field and

receive considerable attention both industrially and experimentally. It has been shown that activated carbon under certain conditions can absorb oxidizing agents, such as halogens, nitric acid, potassium permanganate, potassium dichromate, and ammonium persulfate, and in such condition can be effectively used in the chemical treatment of liquids and gases.<sup>100</sup> Bancroft<sup>101</sup> has discussed the use of oxides in general as oxidizing agents, and Fisher<sup>102</sup> describes the effect of selenium oxide in the oxidation of aromatic side chains, such as the methyl of toluene.

The oxidation-reduction potential for stannous-stannic acid system has been redetermined and the range of data extended.<sup>103</sup> Potassium permanganate was found to give rapid oxidation of the benzene ring of arylboric acid resulting in the formation of phthalic acid.<sup>104</sup> The oxidation of acetylhydrazobenzene by sodium dichromate in glacial acetic acid was studied by Ritter.<sup>105</sup>

The oxidation-reduction reaction of mixed perchloric and sulfuric acids in quantitative analysis has been discussed by Smith.<sup>106</sup> Oxidation-reduction with hydrogen peroxide was studied by Bancroft and Murphy and discussed at length.<sup>107</sup>

The theories relating to autoxidation have long been under discussion and new data are continually being presented in support of the various mechanisms. Thus, Milas<sup>108</sup> and Stephens<sup>109</sup> come to the support of their theories. Egerton<sup>110</sup> has also discussed the mechanism of autoxidation and suggests possible mechanisms of general types of oxidation on the basis of the active molecule theory.

The results of an extensive investigation on the electrochemical oxidation of various organic substances in concentrated aqueous organic salt solutions have been reported.<sup>111</sup> The electrochemical oxidation of toluene in nitric and sulfuric acids has been studied;<sup>112</sup> that of xylose in the presence of alkaline earth bromides and carbonates was studied by Isbell and Frush.<sup>113</sup>

The oxidation of various organic compounds has been reported; thus, vapor phase oxidation of ethanol,<sup>114</sup> propionaldehyde,<sup>115</sup> cinnamaldehyde,<sup>116</sup> hydrazine,<sup>117</sup> mannitol,<sup>118</sup> furan series,<sup>119</sup> autoxidation of animal fats and inhibition,<sup>120</sup> autoxidation of catechol,<sup>121</sup> oxidation of tertiary hydrocarbons with oxygen<sup>122</sup> and others.

The study of atmospheric oxidation was continued by Spoehr<sup>123</sup> in his work on the catalytic oxidation of trioses and related compounds. The mechanism of carbohydrate oxidation was discussed by Swan and Evans<sup>124</sup> as a continuation of the work on this problem.

**Hydrogenation.** Domestic developments in hydrogenation have been confined largely to new researches and primarily to new laboratory preparations.

The heats of hydrogenation of some simple olefins, employing a copper catalyst, have been studied at 82° C.<sup>125, 126</sup> The heat of

hydrogenation of pyridine to piperidine has been determined to be 48,680 cal. per mole over the temperature range 150 to 170° C. In addition, the equilibrium in the gas phase system pyridine, hydrogen, and piperidine was studied at 150 and 170° C., using a nickel catalyst. The free energy decrease for the hydrogenation of pyridine at 150° C. was found to be +3835 cal. per mole, while at 170° C. it was +1760 cal. per mole.<sup>127</sup> The influence of oxygen on the hydrogenation of ethylene was studied. It was found that small amounts of oxygen in ethylene-hydrogen mixtures greatly increased the initial hydrogenation reaction rate for the homogeneous reaction at 538° C.<sup>128</sup>

In the presence of a variety of amines, carbon dioxide and hydrogen under pressures of 200 to 400 atmospheres and temperatures of 80 to 250° C., with Raney nickel or brass catalysts, yielded formates of the amines. It is believed that the amines only serve to neutralize the formic acid formed by the direct hydrogenation of the carbon dioxide; i. e., that the formic acid is produced directly and not through the reduction of compounds formed by the reaction of carbon dioxide and amines. At temperatures above 100° C., the formates of the amines may be dehydrated to the substituted formamides.<sup>129</sup>

The catalytic hydrogenation of nitroguanidine at low pressures with platinum oxide or Raney nickel catalysts has been found to result in satisfactory yields of nitrosoguanidine.<sup>130</sup> Using platinum oxide catalysts and low pressure hydrogenation the  $\delta$ -lactones of aldonic acids have been reduced in good yields to the corresponding sugars. The  $\gamma$ -lactones have also been reduced, but usually gave lower yields of sugars, owing to the further reduction of the sugars to the corresponding sugar alcohols. The sugar alcohols have been obtained in yields of from 60 to 80 percent.<sup>131</sup>

Using a palladium catalyst and low pressure hydrogenation,  $\alpha$ -isomorphine was converted to dihydro- $\alpha$ -isomorphine. In the case of  $\beta$ -isomorphine with a platinum oxide catalyst, two moles of hydrogen were added to yield tetrahydro- $\beta$ -isomorphine, along with the dihydro product.<sup>132</sup> A platinum oxide catalyst and low pressure hydrogen also reduced pseudocodeine methyl ether to tetrahydropseudocodeine as the principal product; the methoxyl group was not eliminated.<sup>133</sup>

The hydrogenation of *cis*- and *trans*-dibenzoyl ethylene was studied, using a platinum catalyst and various solvents. In the case of the *trans*-compound both mono- and unexpected di-molecular products were formed, while in the case of the *cis*-compound the usual expected reduction of the ethylenic double bond took place. Parallelisms between catalytic reductions with hydrogen and reductions with zinc combinations indicated a common reaction mechanism for these two reduction methods.<sup>134</sup>

Dialkyl, diaryl and aryl alkyl ethers were hydrogenated at 175-

200° C. and 150-250 atmospheres with about 5 weight percent of Raney nickel catalyst. The reaction consisted of hydrogenolysis or cleavage of the ether linkage, yielding a hydrocarbon and an alcohol. Depending on the ease of breaking the ether linkage in compounds having unsaturated structures, there may or may not be hydrogenation of the unsaturated linkages along with the ether linkages. The stability of various ethers toward hydrogenolysis is compared.<sup>135</sup>

The electrochemical reduction of sugars to alcohols, e. g., glucose to sorbitol and mannitol was accomplished by Creighton.<sup>136</sup> Lead amalgamated with mercury serves as the cathode and also keeps the catholyte in an alkaline condition. Sorbitol may also be obtained by agitating a neutral solution of glucose under a hydrogen pressure of at least 20 atmospheres at 100-150° C. in the presence of a partially reduced nickel chromate carried on a siliceous material.<sup>137</sup>

**Alkylation.** For convenience alkylated compounds are classified according to the linkage of the alkyl radical to the rest of the molecule. The following classification is used in this survey: alkyl bound to oxygen, to tri- and pentavalent nitrogen, and to carbon or to a metal; when the binding is to the carbon of an aromatic nucleus, it is termed nuclear alkylation.

*Alkyl Bound to Oxygen.* Stoughton, Baltzly, and Bass<sup>138</sup> report the preparation of new alkyl phenols by the Fries migration of phenolic esters and subsequent reduction. Catechol and hydroquinone were first condensed with acid chlorides of fatty acids and then subjected to the aforementioned treatment. Tabulated data are given for a number of new compounds. The simultaneous production of 4- and 2-tertiary alkyl phenols of the benzene series is reported by Perkins, *et al.*<sup>139</sup> The process comprises reacting a *tert*-alkyl halide with a monohydric phenol, having the 2- and 4-positions free, in the presence of aluminum chloride. The similar preparation of *tert*-butylphenol in the presence of hydrated ferric chloride is described by Seymour.<sup>140</sup> Buc<sup>141</sup> suggests the production of alkyl phenols by reacting an olefin, e. g., hexene or cyclohexene, with cresol in the presence of sulfuric acid.

*Alkyl Bound to Nitrogen.* Zimmerli<sup>142</sup> proposes the following procedure for the preparation of alkyl amines. The condensation product of molar proportions of *p*-aminophenol and furfural is treated with dimethyl sulfate in chlorobenzene at 60° C. for two hours. The crystalline addition compound is dissolved and reacted with a mixture of 95 percent sodium carbonate and 5 percent sodium sulfite, whereby furfural is liberated and monomethyl-*p*-aminophenol is obtained. According to Carleton and Woodward<sup>143</sup> mono- and diethylanilines are obtained by autoclaving at 180-185° C. 465 parts by weight of aniline, 208 parts of ethyl

chloride and 250 parts of ethanol. The same investigators<sup>144</sup> effect a similar synthesis by reacting ethanol, aniline and hydrogen chloride under pressure at 180-185° C. Clarke and coworkers<sup>145</sup> produced tertiary amines from simple aliphatic amines by reacting with methanol and formaldehyde; yields in excess of 80 percent are reported.

*Nuclear Alkylation.* Thomas<sup>146</sup> produces higher alkyl derivatives of aromatic compounds by partially chlorinating an aliphatic hydrocarbon of eight or more carbon atoms and then reacting this mixture with an aromatic compound in the presence of a Friedel and Crafts condensing agent. Another method for producing alkylated aromatic compounds is suggested by Isham.<sup>147</sup> Propylene gas, for example, is led into a mixture of naphthalene and naphthalenesulfonic acid at 120° C. until the desired absorption is effected. The propylated naphthalene separates as a clear yellow layer when the reaction mass is treated with hot water. Ipatieff and Komarewsky<sup>148</sup> obtained ethylbenzene and biphenyl in rather small yields by autoclaving benzene and dry hydrogen chloride at 125° C. Destructive hydrogenation occurred, giving ethane, which then alkylated the ring.

*Alkyl Attached to Metal.* Calcott and coworkers<sup>149</sup> suggest that the subsidence of pressure be used as a guide for controlling the reaction between large amounts of lead mono-sodium alloy and alkyl chloride. With respect to the preparation of tetraethyl lead, a small proportion of the total ethyl chloride required is first added to the surface of the alloy and then other portions are added as the reaction pressure abates.

**Esterification.** The preparation of esters has, in all probability, been the most active field of organic research in recent years. The development of new and important esters of carbohydrates, the expanded use of the higher fatty acids, and the economic introduction of many new acids and alcohols suitable for the production of solvents and plastics have contributed to increase the technical and patent literature on the subject of esterification. An adequate discussion of all types of esters cannot be made here. Some, such as the esters of cellulose, will be omitted entirely.

*Phosphoric Acid Esters.* Levene and Schormüller<sup>150</sup> have studied the phosphoric esters of hydroxyamino acids, e. g., 1-hydroxyprolinephosphoric acid. Tritolyl phosphates were prepared by reacting cresol successively with either phosphorus pentachloride or pentoxide.<sup>151</sup> The production of mixed esters, by reacting various phosphoric acids with a mixture of alcohols obtained by the reduction of fatty oils, is described by Graves<sup>152</sup>

Tremendous progress has been made during the past few years in the preparation of mineral acid esters of alcohols, e. g., by reacting olefins obtained from refinery wastes with sulfuric acid. Wilson<sup>153</sup> reports the procedure for the preparation of ethyl



acetate, which consists in hydrolyzing the reaction product of ethylene and sulfuric acid to decompose all the diethyl sulfate present and then adding calcium acetate, while maintaining an excess of free sulfuric acid or monoethyl sulfate. Similar processes relating to the preparation of isopropyl and butyl esters are also described.<sup>154</sup> Such esters may also be obtained by heating the carboxylic acid with the olefin in the presence of sulfuric acid and permitting the reaction mixture to stratify into a solvent phase containing the ester and an acid phase.<sup>155</sup> Another modification consists in reacting olefins, having less than seven carbon atoms, with lower fatty acids, above the boiling point of the ester and in the presence of halides of zinc, aluminum, etc., or relatively nonvolatile inorganic acids, such as sulfuric or phosphoric acids.<sup>156</sup> Vail<sup>157</sup> shows that similar esters can be produced by reacting an olefinic hydrocarbon, e. g., propylene, carbon monoxide, and an alcohol under pressure.

Mono- and dicarboxylic acids have been employed extensively in the preparation of esters. Oxalic and malonic acids, esterified with an excess of ethyleneglycol at 100° C., produce formic and acetic esters, respectively.<sup>158</sup> When an alkylene diester, such as ethyleneglycol diacetate, is treated with ethanol in the presence of hydrogen chloride, ethyl acetate and ethylenechlorohydrin are formed.<sup>159</sup> The esterification of dicarboxylic acids, such as adipic, methyladipic, pimelic, sebacic, muconic, zeronic, etc., with ether-alcohols is described by Izard.<sup>160, 161</sup>

Alcohols derived by the hydrogenation of oils<sup>162-164</sup> may be esterified by suitable acids to produce didodecyl adipate and phthalate, tridodecyl citrate, dimyristyl succinate, etc., by reacting in the presence of a water-removing agent or carrier, e. g., sulfuric acid or benzene. Numerous esters of levulinic acid and alcohols such as octyl, nonyl, cyclohexanol, etc., are described by Lawson and Salzberg,<sup>165</sup> while terpene esters of phthalic acid are reported by Borglin.<sup>166</sup>

The esterification of polyhydric alcohols with anhydrides of dicarboxylic acids in the presence of pyridine is described by Malm and Fordyce<sup>167</sup> and a study of the esterification of glycerol with chloro- and trichloroacetic acids is reported by Helgeson and Shaw.<sup>168</sup> It is also shown that glycerol or glycols may be esterified by a ketene in the presence of sulfuric acid.<sup>169</sup>

The preparation of vinyl esters of lower aliphatic carboxylic acids is described by Perkins.<sup>170</sup> The conditions for the synthesis of vinyl acetate from acetic anhydride and paraldehyde are given.

The preparation of aromatic esters has been studied by a number of investigators. Nitrobenzyl esters of organic acids have been studied by Kelly and Segura.<sup>171</sup> The formation of tolyl phthalates from cresols and phthalic acid is described in one patent<sup>172</sup> and

the preparation of benzyl esters of halogeno-*o*-benzoylbenzoic acids in another.<sup>173</sup>

The acetylation of sucrose has been reported by Cox and Ferguson;<sup>174</sup> sucrose is treated with acetic anhydride in the presence of about a third part of sodium acetate which serves as a catalyst.

**Hydrolysis.** Some notable advances in technical hydrolytic operations have been reported during the past year.

Downing and coworkers have investigated the preparation of *o*-dihydroxybenzenes from the corresponding dihalogen derivatives. It was found that the introduction of a reducing agent, such as sodium formate,<sup>175</sup> to the reacting materials,  $C_6H_4Cl_2$ , NaOH (31 percent),  $BaCl_2$ , and  $Cu_2O$ , gave good yields of the phenolic compound. The gradual introduction of aqueous sodium hydroxide during the course of the run,<sup>176</sup> so as to maintain the alkali concentration at about 2.9 normal, was found to be advantageous; the feasibility of making the process continuous was also indicated.<sup>177</sup> When a barium hydroxide concentration of 2.44 normal is used and the charge is heated at 275° C. for 10 hours, a yield of 69.7 percent of catechol was obtained.<sup>178</sup>

Britton<sup>179</sup> has discovered that when an *o*- or *p*-monochlorinated aromatic hydrocarbon, having the general formula  $R-C_6H_4-Cl$ , wherein R represents an aryl or alkyl group (e. g., chlorobiphenyl or chlorotoluene), is treated at about 360° C. with 10 percent sodium hydroxide, a substantial portion of the product is a *m*-hydroxy derivative. *o*-Chlorotoluene under such conditions yields 77 percent of cresols, consisting of 59 percent *m*- and 41 percent *o*-cresol. Moose<sup>180</sup> has shown that when a mixture of monochlorobiphenyls, preferably the eutectic (25 percent 4-chloro- and 75 percent 2-chloro-), m. p. 14° C., is similarly treated, the product will contain from 35 to 50 percent of the *m*-hydroxy derivative, the remainder being almost wholly 2-hydroxybiphenyl.

Britton and Stoesser<sup>181</sup> report on the conversion of  $\alpha$ -bromonaphthalene to  $\alpha$ -naphthol by reacting with 15 percent sodium hydroxide at 225° C. When, however,  $\alpha$ -chloronaphthalene is treated in an iron autoclave with 10 percent sodium hydroxide at 360° C., the product contains both  $\alpha$ - and  $\beta$ -naphthols in about equal proportions.<sup>182</sup>

Bannister<sup>183</sup> has demonstrated that a group of organic acids, consisting of formic, acetic, oxalic, and succinic acids, can be obtained from cellulose-containing materials by fusing such materials with caustic soda at 200-260° under pressure. When corn cobs are treated with about an equal quantity by weight of caustic, a typical yield of acids based on the weight of corn cobs (containing 7 percent moisture) is as follows: Acetic 25, oxalic 30, formic 15, and succinic 10 percent.

The production of indanthrones, particularly the technically important *N*-dihydro-1,2,1',2'-anthraquinoneazines from 2-amino-

anthraquinone, has received considerable attention. In addition to the usual caustic alkali and oxidant, Bishop and Perkins<sup>184</sup> recommend the incorporation of butyl alcohol and sodium phenolate to the fusion mixture. Murch<sup>185</sup> suggests the addition of alkali metal chlorates and nitrates with 2-aminoanthraquinone as an aqueous slurry to the fused caustic alkali. Thompson<sup>186</sup> has developed a procedure involving the treatment of 2-aminoanthraquinone with a caustic melt in the presence of sodium phenolate and an alkali salt of a lower fatty acid. A procedure for the separation of the azine from the fusion mass is reported by Peck and Knowles.<sup>187</sup>

The preparation of monohydroxy alcohols by the hydration of olefins has been investigated by Larson.<sup>188</sup> In the proposed process the olefin and steam react in the presence of a volatile halide, e. g., ammonium chloride, and activated charcoal.

The addition of a relatively small amount of soap is proposed to prevent the formation of a hard scale of magnetic iron oxide on the reactor walls in the hydrolysis of chlorobenzene.<sup>189</sup>

**The Friedel and Crafts Reaction.** Substantial progress has been made during the past few years in our understanding and application of the Friedel and Crafts reaction.

Groggins and his coworkers have carried out extensive investigations in the preparation of ketones by condensing aromatic compounds with carboxylic acids, their anhydrides, and acid chlorides. Studies with Nagel and Stirton<sup>190</sup> and subsequently with Newton<sup>191</sup> showed that carboxylic acids, e. g., acetic and benzoic, could be used instead of the acid chlorides or anhydrides. In some of these investigations<sup>192</sup> it was found that the addition of powdered aluminum or iron exerted no marked deleterious effect<sup>193</sup> and the use of iron alloy reactors was suggested.<sup>194</sup> It was also found that both acyl groups of acid anhydrides could be made to enter into reaction<sup>195</sup> when three or more moles of aluminum chloride are used, thus doubling the yield of ketones. A theory regarding the mechanism of reaction in the condensation of carboxylic acids and their anhydrides is set forth.<sup>196</sup>

Gilman and his colleagues have continued their investigations in the furane series. Studies with Calloway and Burtner<sup>196</sup> showed that furfural and isopropyl chloride gave 4-isopropyl-2-furfural. Gilman and Burtner<sup>197</sup> discuss certain anomalous reactions, and in a further investigation with nitro compounds,<sup>198</sup> it was found that nitrofuran, propionyl chloride, and titanium tetrachloride gave 5-chloro-2-furyl ethyl ketone. Nitrobenzene, however, undergoes reduction and chlorination when treated with isopropyl bromide and aluminum chloride to give *o*- and *p*-chloroanilines.

Machlis and Blanchard<sup>199</sup> report that 4-propiobiphenyl, and not the 3-isomer as previously reported, results when biphenyl

and propionyl chloride are permitted to react in the presence of aluminum chloride. Silver and Lowy<sup>200</sup> have condensed biphenyl with acetyl chloride and dichloroacetic anhydride to obtain *p,p'*-diacetylbiphenyl and chloromethyl *p*-xenyl ketone, respectively. With phosgene, a mixture of di-*p*-xenyl ketone and *p*-xenil was obtained and with thionyl chloride *p*-xenyl-*p*-sulfinylbiphenyl was the principal product.

Dougherty and Hammond<sup>201</sup> have studied the reaction between benzene and sulfur in the presence of aluminum chloride; diphenyl sulfide and thianthrene were formed, the percentage of the former increasing with the ratio of aluminum chloride used.

Stoughton<sup>202</sup> has reported on Fries' migrations with esters of  $\alpha$ -naphthol. The propionate under the influence of aluminum chloride yields 54 percent of the 2-propionyl, 6 percent of the 4-propionyl, and 2 percent of the 2,4-dipropionyl derivative. Other esters give similar products. Sekera<sup>203</sup> has found that ferric and zinc chlorides can be used instead of aluminum chloride to effect transformation of aryl esters of carboxylic acids into hydroxyaryl ketones.

It has been shown that olefins and cyclic compounds can be condensed in the presence of either  $\text{BF}_3$  or  $\text{AlCl}_3$ ;  $\text{C}_3\text{H}_8$  with benzene yields mono- to tetra-isopropyl derivatives.<sup>204</sup>

In the preparation of alcohols, e. g.,  $\beta$ -phenylethyl alcohol from ethylene oxide and benzene, Carpenter<sup>205</sup> discovered that the introduction of air greatly improved the yields.

**Polymerization.** *Theoretical.* A number of valuable articles have appeared which deal with newer polymerizations and their reaction mechanisms. Theoretical studies of such important resin-forming reactions as those between urea or phenol and formaldehyde continue to be neglected.

The polymerization of divinylacetylene by heat has been shown by Cupery and Carothers<sup>206</sup> to involve the formation of cyclobutane derivatives, 1,2-divinylethynyl cyclobutane being the dimer and bisvinylethynylcyclobutylacetylene the probable trimer. Dykstra<sup>207</sup> has demonstrated a similar mechanism for the heat polymerization of vinylacetylene.

Marvel and co-workers<sup>208, 209</sup> have prepared polysulfones of high molecular weight from olefins and sulfur dioxide in the presence of oxidizing catalysts; these polysulfones appear to be linear polymers terminated by hydroxyl groups. Other linear polymers of interest are the polymeric formals of Hill and Carothers<sup>210</sup> the polymeric decamethylene oxide of Hill,<sup>211</sup> and the linear ammonium salts described by Gibbs and Marvel.<sup>212</sup>

Catalysts which seem destined to become of increasing importance for polymerization reactions are phosphorous pentoxide<sup>213-215</sup> and boron trifluoride and its derivatives.<sup>216, 217</sup> The acceleration of polymerization by extreme pressure (6000 atmospheres)

was determined by Starkweather<sup>218</sup> for a large number of substances; it was observed that the polymers thus formed differ little from those obtained under more nearly normal conditions. Thompson and Burk<sup>219</sup> found that, in the substantial absence of oxygen, citral and heptaldehyde do not polymerize, while styrene continues to polymerize at a diminished rate, catalyst effects still being predominant.

*Applications.* While no strictly new resin seems to have come into general commercial use, new applications and improvements of well known resins are of much interest.

Phenol-formaldehyde resin, in the form of the colloidal plywood glue described by Sontag and Norton,<sup>220</sup> fills the need of the plywood industry for a waterproof and vermin proof bond. Translucent and transparent cast phenolic resins meet a demand for a durable material of extreme beauty.<sup>221</sup> Phenolic resin with a mineral filler is well adapted to the fabrication of acid-proof chemical equipment.<sup>222</sup>

Oil soluble resins of various types are finding wider use in the varnish and paint industries<sup>223, 224</sup> to give films which are more durable, faster drying, more stable in color, or more resistant.

Improvements in molding technique have brought about increased use of thermoplastic resins. Plasticized vinyl halide resins<sup>225</sup> have formed the basis for thermoplastic molding materials of a wide range of properties. Likewise, the technique of isomerizing rubber to tougher and less extensible products has been improved, and a light colored thermoplastic material,<sup>226</sup> similar in properties to hard rubber, has been made from rubber by the use of tin halides. Both the above resins have remarkable resistance to ordinary chemical reagents.

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## Chapter XXV.

### Chemical Economics.

(1931-1935)

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No marked increase in quantity or quality of publications on chemical economics has occurred since the first review appeared in the "Annual Survey" (Volume V, Chapter XL, 1931). Only two major events have occurred to indicate a more general interest in the subject: the American Chemical Industries Tercentenary in New York under the chairmanship of A. W. Hixson in 1935, and the Silver Anniversary of the American Institute of Chemical Engineers in Chicago in 1933. During the Tercentenary celebration special chemical issues were published by *The Wall Street Journal*<sup>1</sup> and the *Boston Evening Transcript*.<sup>2</sup> Also, a general symposium on chemical economics was arranged by R. P. Soule, and a plan was carried out to have a paper of economic interest scheduled in each divisional program. At the time of the Chemical Engineers' Anniversary, a symposium<sup>3</sup> was published on economic and technological progress in the process industries during the period 1908-33.

Although a sustained, marked expansion of interest in chemical economics does not seem to be widespread, it must be emphasized that the editors of the industrial journals are making every attempt to foster the growth of this subject. A gradually increasing stream of chemical thought is flowing into the torrent of financial and economic literature. Some of the larger financial houses are employing chemically trained men, and in some cases economists have entered the service of chemical companies. The publication of "Chemical Economics"<sup>4</sup> by Haynes should serve as a crystallizing force on chemico-economic concepts, and the popular version of this work—"Men, Money and Molecules"<sup>5</sup>—will undoubtedly transmit an interest in the business side of chemicals to a numerous lay public.

Five major factors are responsible for the present unorganized condition of chemical economics. First, the hybrid chemist-economist is not easily developed; the chemist appears to be the more likely parent stock. Second, the individual chemical industries are so diverse that it is difficult to find a common economic ground. Third, the rate of

\* Grateful acknowledgment is made of helpful suggestions and comments from R. T. Baldwin, C. C. Concannon, T. W. Delahanty, W. A. Hamor, Williams Haynes, S. D. Kirkpatrick, A. E. Marshall, D. P. Morgan, and W. N. Watson.

change in technology is much more rapid than in other industries that have been subjected to extensive economic analysis. Fourth, there is a real need for a chemical imagination less fanciful than that reflected in the lay press; pseudo-economic reasoning can produce shapes that are far distorted, without an added torque from chemical fiction. Finally, there are at the present time few reliable statistics on which a sound structure for the subject can be built; until such time as the industry shall make adequate information available, efforts in this direction will be severely handicapped.

It is safe to prophesy, however, that eventually a rounded philosophy of chemical economics will be evolved through mutual effort of the chemist and the economist. It is the writer's hope that this survey of the literature may stimulate that progress and mark a milestone on the road.

**Publications of a General Nature.** The editors of our industrial journals—Williams Haynes, H. E. Howe, S. D. Kirkpatrick, L. E. Westman, and their associates—maintain a running fire of economic comment on timely topics. Their annual review numbers, especially in the case of *Chemical and Metallurgical Engineering*, are in a sense textbooks of chemical economics.

Haynes, in "Chemical Economics,"<sup>4</sup> devotes chapters to chemical supply and demand; cost, value, and price; chemical distribution; cartels and consolidations; and American chemical mergers; in addition, the historical background of the industry is covered in considerable detail. In "The Development of American Industries,"<sup>6</sup> brief economic reviews are given of the following industries: pulp and paper, textiles, rubber, leather, petroleum, glass, cement, chemicals, and paint, varnish, and lacquer, as well as several metals. The broad scope of "Twenty-Five Years of Chemical Engineering Progress"<sup>3</sup> has already been mentioned. Weidlein and Hamor, in "Science in Action,"<sup>7</sup> in addition to reviewing the part that research has played in the development of various industries, discuss the economic importance of research in problems of waste utilization, engineering economics, industrial management, employment and banking, and in the creation of new industries.

In recent years studies by various state planning boards and universities have brought to the surface critical problems affecting industrial structure, such as freight rates, raw materials, markets, power, and water supply. Such activities have been particularly noteworthy in mineral technology; the State Planning Reports of Illinois and Colorado have advised closer study of the requirements of consumers in order to improve marketing, and searches for new uses have been begun in Michigan. Research on the development of new industries has been advocated in many studies of this nature.<sup>8</sup>

Other subjects of a general nature which have been discussed include: the relation of chemical industry to the state,<sup>9-15</sup> to the individual,<sup>16, 17</sup> to other industries,<sup>18</sup> to other sciences,<sup>19</sup> to warfare,<sup>20, 21</sup> and to the tariff;<sup>22, 23</sup> the chemical industry during the depression;<sup>24-32</sup> the chemi-

cal industry and inflation;<sup>33-36</sup> and the chemical industry of the future.<sup>37-40</sup>

**Education in Chemical Economics.** The desirability of training in economics for engineering students is generally admitted by educators,<sup>41, 42</sup> as shown by the following quotation from a report by the Society for the Promotion of Engineering Education.<sup>43</sup> This point of view is further emphasized by the Engineers' Council for Professional Development.

"There seems to be rather general agreement that more than the present emphasis on economics and its application in engineering should be given; that sufficient time is now devoted to the subject of general economics as taught by the Departments of Economics; and that it would be desirable both to provide for specific instruction in engineering economics, and to devote greater attention and emphasis to economic phases of engineering problems in the engineering subjects themselves."

A survey of the curricula of institutions accredited by the American Institute of Chemical Engineers indicates that these recommendations are, in general, being followed. Practically all these schools list general economics as a required course or as a preferred elective. Economic aspects of chemical engineering problems are usually emphasized in the engineering courses, and Tyler's monograph,<sup>44</sup> which unfortunately has not been enlarged or revised since its publication ten years ago, has been used as the basis of an organized course. Read<sup>45</sup> has included a chapter on chemical economics in his textbook on industrial chemistry; Haynes' monograph<sup>4</sup> is being used as a text and as assigned supplementary reading. "Economic Balance" has for a number of years been included in the chemical engineering curriculum at Massachusetts Institute of Technology, and, in one form or another, in many other institutions.

In chemical curricula, as distinguished from chemical engineering curricula, much less emphasis is placed on economics. Some schools, however, recommend the subject as an elective. It is to be hoped that there will be an increasing trend in this direction.

**Research in Chemical Economics.** Professional economists still practically ignore the chemical industry as a field for research. In most cases in which data on chemicals have been studied, they have been included as part of the manufacturing industries as a whole, and not as a subject of interest in their own right. As an example of the general situation, the thirty-second annual list<sup>46</sup> of doctoral dissertations in political economy in progress in American universities and colleges, which includes a total of 537 titles, contains none covering chemicals, in the narrow sense of the word, one each on the steel, tire, and drug industries, and two on the ceramic industry.

The chemist, on the other hand, appears to be gradually becoming more and more interested in the economics of his industry. We can look forward with confidence to an increasing number of researches by chemical economists entering the profession from the chemical side.

**Economic History.** Many of the references cited in other sections are concerned to a considerable extent with the economic history of chemical manufactures. For example, "Twenty-five Years of Chemical Engineering Progress"<sup>3</sup> includes historical discussions of the more important process industries during the period 1908-33 and a statistical review of the entire group by Weidlein and Bass. Haynes<sup>4, 5</sup> and Weidlein and Hamor<sup>7</sup> likewise include much valuable historical material on industrial development in their treatises.

Browne<sup>47</sup> has traced the early history of the chemical industry in New York. Haynes and Bass<sup>48</sup> have recorded in chronological form the outstanding economic and technical developments in the industry during the last three centuries. Histories of individual chemical companies have been published in *Chemical Industries*,<sup>49</sup> *Industrial and Engineering Chemistry*,<sup>50</sup> and *Fortune*.<sup>51</sup>

**Sources of Statistics.**<sup>52</sup> The most important sources of statistical data on the chemical industry are included in the following list.

*General.* Miscellaneous publications and releases from the Chemical Division, Bureau of Foreign and Domestic Commerce (activities have been described in detail by Concannon and Delahanty).<sup>53</sup> Tariff Information Surveys issued by the Tariff Commission in 1921 and 1929.

*Production and Sales.* Census of Manufactures (biennial), including mimeographed preliminary sheets and printed finals on divisions of the industry. Minerals Yearbook (annual). Census of Dyes and Other Synthetic Organic Chemicals (annual), U. S. Tariff Commission; the 1934 issue contains for the first time reports on "inorganic chemicals used in the production of coal tar products." Sulphuric Acid and Superphosphate (monthly), Bureau of the Census. Production of Methanol (monthly), *ibid.* Statistics on Industrial and Beverage Alcohol (annual); Statistics of Industrial Alcohol (monthly); Bureau of Internal Revenue.

*Hours and Wages.* Trend of Employment, Department of Labor. Survey of Current Business, Department of Commerce. Federal Reserve Bulletin (monthly). Reports of the Chemical Alliance.

*Prices.* Wholesale Prices, Department of Labor. Survey of Current Business, Department of Commerce. Federal Reserve Bulletin. *Oil, Paint and Drug Reporter. Chemical Industries.*

*Distribution.* Census of Manufactures and Minerals Yearbook contain some meager data. (With the 1935 Census of Manufactures schedule is appended a Census of Distribution schedule which specifically covers a few chemical groups: agricultural insecticides, alkaloids, etc.) Printed reports, Tariff Commission, under section 315, Tariff Act of 1922, and section 336, Tariff Act of 1930; for the products covered, the data are very complete. Census of Wholesale Distribution, 1929, Bureau of the Census (very little on chemicals). Census of American Business, 1933, Bureau of the Census. Tariff Commission press release on salt. World Trade Notes, Chemical Division, Bureau of Foreign and Domestic Commerce.

**Consumption.** Census of Manufactures. Annual review and statistical issues of *Chemical & Metallurgical Engineering* present detailed data for a number of heavy chemicals. Minerals Yearbook contains some consumption statistics. Sulphuric Acid (monthly), Bureau of the Census. National Fertilizer Association; data for acid, phosphate, nitrogen, and potash.

**Exports and Imports.** Foreign Commerce and Navigation of the U. S. (annual), Department of Commerce. Monthly Summary of Foreign Commerce of the U. S., preliminary, Department of Commerce. Advance official data mimeographed sheets (monthly), Chemical Division, Department of Commerce. U. S. Foreign Trade Statistics (monthly), Bureau of Foreign and Domestic Commerce (shows imports only). (The utility of United States foreign trade statistics, with suggestions for their improvement, has been discussed in detail by Mears.)<sup>54</sup>

**Finance.** No official publication has much information on finance as applied specifically to the chemical industries. Survey of Current Business contains considerable financial statistics. Federal Reserve Bulletin is a fundamental source. *Chemical Markets (Chemical Industries since Oct., 1933)*. Annual reports of individual chemical companies.

**Construction.** Monthly summaries in *Chemical & Metallurgical Engineering*. (Sources of information on construction and employment in construction have been described in detail by Gill).<sup>55</sup>

**Foreign Countries.** The larger countries collect official statistical material in a similar manner. In many cases statistical yearbooks are published. Canadian data collected by the Dominion Bureau of Statistics have been summarized by Losee and McLeod.<sup>56</sup> Periodic reviews of the more important foreign countries from the point of view of chemicals have been published by the Chemical Division, U. S. Bureau of Foreign and Domestic Commerce.<sup>57</sup>

**Technological Research and Development.** The ultimate source of new economic developments in the chemical industries lies in the research laboratories. As an example of the importance of sustained research, a recent news release from the General Electric Company stated that, during the five depression years 1930-1934, the ratio between business attributable to "new" lines of products (i. e., lines not manufactured more than ten years prior to the year under consideration) and total business for all lines manufactured by that company, was, on the average, approximately 10 percent higher than for the five prosperity years 1926-1930. The achievements that have come as a result of research have been discussed in detail by Boyd,<sup>58</sup> by Redman and Mory,<sup>59</sup> and by Weidlein and Hamor.<sup>7</sup>

According to a compilation by West and Hull,<sup>60</sup> there were 1575 industrial and consulting laboratories in the United States in 1933. Holland and Spraragen<sup>61</sup> found that the tendency to decrease research expenditures during the depression, while not marked in 1931, increased

progressively during 1932 and 1933;\* further, that the major emphasis on research has been changed from attempts at lower production costs to the development of new products, new uses, new processes, and the improvement of existing products.

Informative surveys of current practice in research laboratory management have been conducted by Ross<sup>62</sup> and by the Metropolitan Life Insurance Company.<sup>63</sup> Additional discussions of various aspects of research management have appeared on: laboratory information service,<sup>64</sup> financing,<sup>65</sup> expenses,<sup>66</sup> objectives,<sup>67</sup> and personnel.<sup>68</sup>

Special attention has been accorded the use of pilot or semi-works plants as an effective development procedure.<sup>69-71</sup>

The research chemist should be particularly well-informed on patent matters, because the literature available to him is excellent. It includes monographs by Deller,<sup>72</sup> Geier,<sup>73</sup> Rhodes,<sup>74</sup> Rivise,<sup>75</sup> Rossman,<sup>76</sup> and Toulmin;<sup>77</sup> a section by E. J. Prindle in the "Chemical Engineers' Handbook";<sup>78</sup> the patent index by Worden;<sup>79</sup> the report on the patent system by the Science Advisory Board;<sup>80</sup> and a number of journal articles.<sup>81-94</sup>

A survey has been made of the respective merits of exclusive and non-exclusive licensing of patented inventions.<sup>95</sup> Weidlein and Bass<sup>96</sup> have pointed out that a comparatively low monetary valuation is set on patents and goodwill by chemical companies.

Three additional related subjects have been discussed: the chemical expert,<sup>97</sup> engineering contracts,<sup>98</sup> and competition between university research and consultants.<sup>99</sup>

**Raw Materials.** Emeny<sup>20</sup> and Zimmerman<sup>100</sup> have provided valuable source books of information on raw materials, including those used by the chemical industries. Weber and Alsberg's<sup>101</sup> monograph on vegetable shortenings is not only a masterly treatment of this industry, but also a model to be followed in similar studies of a technico-economic nature. Several discussions of miscellaneous substances as chemical raw materials have appeared: agricultural products,<sup>102</sup> cellulose,<sup>103</sup> fish and animal oils,<sup>104</sup> lead,<sup>105</sup> chemical raw materials in petroleum refining,<sup>106, 107</sup> phosphate rock,<sup>108</sup> and vegetable oils.<sup>109</sup> Special mention should be made of the 8 page supplement to the January, 1934, issue of *Chemical & Metallurgical Engineering* entitled "New Data on Chemical Raw Materials for the Process Industries."

Much interest has recently been aroused in the possibility of closer relationship between the chemical industry and agriculture, particularly from the point of view of increased use of agricultural products as raw materials for chemicals. Many ideas have been suggested by Hale,<sup>110</sup> but there has been considerable criticism of his views.<sup>111</sup> In 1935 a conference was held in Dearborn, Mich., for the purpose of discussing means of effecting closer economic cooperation between agriculture, industry, and science.<sup>112</sup> This conference eventuated in the

\* Since this survey was completed, the tendency has, in general, been reversed.—L. W. B.

organization of the Farm Chemurgic Council, which has begun activities along the lines indicated.

**Chemical Technogeography.** The location of factories of all types has in the past, with few exceptions, been more a matter of chance than of selection based upon careful study of the various factors involved.<sup>113</sup> Chemistry has an intimate connection with the problems of highway transportation, which, especially within the past two decades, has changed profoundly merchandising methods, operations, and even plant locations. The advent of the pipe line has been of notable economic significance, and its future developments may be even more striking. In the last half-century the production and distribution of electricity has become a major American industry, and the resulting increase in mobility of energy has removed many restrictions on plant location and layout and the design and control of machinery and processes.

An excellent summary of economic factors to be considered in chemical plant location has been prepared by Cuno as a chapter in the "Chemical Engineers' Handbook."<sup>78, 114, 115</sup> The twelve governing factors discussed are: raw materials; fuel; power; water; labor; transportation; freight rates; markets; consumer, feeder, and competitive industries; climate; taxes and corporation fees; and state and municipal restrictions. A bibliography on plant location containing 272 references has been prepared by Perry and Cuno.<sup>116</sup> The economic factors governing the choice of locations for major chemical plants recently built in the South have been reviewed by Kirkpatrick<sup>117</sup> and by Haynes.<sup>118</sup> Other summaries of chemical activities in various geographic regions have been made for New England,<sup>119</sup> the Far West,<sup>120, 121</sup> the South,<sup>122, 123</sup> and the South-west.<sup>124</sup>

**Chemical Engineering Economics.** Tyler's monograph,<sup>44</sup> although bearing the title "Chemical Engineering Economics," broadly covers not only the engineering phases of chemical processes, but also the entire field of chemical economics. The recent developments in the more strictly engineering aspects have also been treated in sections of reviews of chemical engineering progress which have become a feature of recent volumes of the "Annual Survey." To avoid duplication, mention of work in this field, except as covered in other sections, will be limited to pointing out the economic importance of such subjects as feasibility of processes and products,<sup>67</sup> plant design and equipment choice,<sup>78, 125, 126</sup> economic balance, and amortization and depreciation.<sup>127, 128</sup>

**Production.** In a comprehensive survey of the nation's productive capacity, Nourse<sup>129</sup> found that, on the average, our entire manufacturing industry was operating during 1925-29 at approximately 80 percent of practical capacity. He cites the coke industry as the best illustration of slow displacement of obsolescent capacity by a more efficient process; in 1930 only 29 percent of beehive capacity was utilized, while in normal times 85 to 90 percent of by-product oven rated capacity was used. Surplus capacity in petroleum refining is



uncertain in amount, but there is no evidence of an increase in excess capacity. In the period 1925-29 capacity was utilized in portland cement manufacture to the extent of 80 percent, in the rayon industry close to 100 percent, in steel production 93 percent, and in plate glass manufacture 85 percent.

Using data compiled by Mills<sup>130</sup> for a large group of individual industries, Weidlein and Bass<sup>96</sup> pointed out that, in nearly all the 14 process industries included in the list, there has been a notable increase in physical volume of production<sup>131, 132</sup> and in physical volume of production per wage earner. There has been a marked decrease in cost of materials per unit of product in the post-war period and a similar change in the labor costs.

Alford and Hannum<sup>133</sup> have shown that there may be startlingly large variations in production per kilo-man-hour in establishments devoted to the manufacture of the same products, as, for example, in petroleum refining. Labor costs in the chemical industry have been analyzed.<sup>134-136</sup>

**Prices.**<sup>137</sup> Warren and Pearson,<sup>138</sup> in a study of wholesale prices of basic commodities in the United States for the period 1797-1932, found a striking decline, compared with all commodities, in the prices of the chemical-and-drug group (Table I).

TABLE I. *Index Numbers of Wholesale Prices*  
1910-1914 = 100

	All Commodities	Chemicals and Drugs	Farm Products	Foods	Hides and Leather	Textiles	Fuel and Lighting	Metals and Metal Products	Building Materials
1800	129	427	99	157	62	225	159	322	51
1813	162	848	104	172	77	291	334	419	63
1830	91	207	58	94	85	181	116	209	47
1850	84	154	71	84	67	116	95	147	61
1865	185	300	148	180	152	266	214	306	118
1880	100	120	80	96	113	128	92	166	81
1900	82	101	71	79	77	95	88	115	84
1918	191	225	208	185	195	244	207	160	179
1920	226	203	211	213	266	293	311	175	272
1930	126	110	124	141	155	143	149	108	163
1932	95	91	68	95	113	99	133	94	130

Using the prices during the period 1910-14 as a base, it is seen that, until the close of the World War, chemicals and drugs were one of the highest priced commodity groups. A marked decreasing trend in the index numbers is clearly apparent, however, throughout the period covered. The effect of war-time demand on chemical prices is illustrated in the figures for 1813, 1865, and 1918. Since 1918, prices for chemicals have dropped sharply, and were lower in 1932 than the indexes

for any other group of manufactured commodities, or than the index for all commodities; they were even lower than during the period preceding the War. It should be noted that in spite of this sustained trend toward lower prices, the chemical industry has maintained an outstanding record of financial return.

The prices of chemicals are not likely to rise during the next ten years as rapidly as the general commodity index, according to Copeland.<sup>34</sup> Pricing has not been reduced to a scientific basis, but there are various applicable analytical methods that are of great assistance.<sup>139-141</sup> National monetary adjustments are most likely to be effective in changing the prices of commodities that enter into international trade or that are traded on commodity exchanges.<sup>142</sup> Laufer<sup>143</sup> has pointed out the important bearing on chemical prices of supplantive competition, new synthetic developments, and the protectionist policies of nations.

**Fuel and Power.** McBride,<sup>144</sup> introducing a symposium on fuel and power sources from the point of view of the chemical engineer, has pointed out that the process industries paid for almost half the fuel and energy used in American factories in 1929. This is a notable increase over the proportion in 1909.<sup>96</sup> McBride further states that the consumption of coal, the most abundant and cheapest fuel, is gradually decreasing as a result of more efficient use and because of competition from other fuels. Oil now furnishes over 25 percent of the energy supply, while as recently as the World War it accounted for only about 10 percent. In Table II is given an estimate of the probable importance of various energy sources in the United States in 1940.

TABLE II. *Energy Sources of American Industry*

	Average 1923-27 B. t. u. (Trillions)	Percentage of Total	Estimated for 1940 B. t. u. (Trillions)	Percentage of Total
Anthracite coal .....	2,000	8	1,500	5
Bituminous coal .....	14,000	60	15,500	48
Petroleum .....	5,000	20	8,000	25
Natural gas .....	1,500	6	5,000	16
Water power .....	1,500	6	2,000	6
	<hr/> 24,000	<hr/> 100	<hr/> 32,000	<hr/> 100

Many state planning boards have analyzed their power situations. Minnesota, Missouri, Arkansas, Indiana, Wisconsin, Iowa, Colorado, Texas, Washington, Maine, and Pennsylvania have studied their electric power resources quite broadly. The Maine State Planning Board published a bulletin dealing with markets for power, such as electro-metallurgy and fertilizer and chlorine manufacture. Similar studies have been published for Missouri, Oregon, and the Pacific Northwest.

**Merchandising Research.**<sup>145</sup> Commercial or merchandising research has received a new impetus, which is especially noticeable in the marketing of chemicals, through the use of the laboratory as an

adjunct to market analysis. Switz,<sup>146</sup> referring to the standard recommendation for diversification and development of new products so frequently made to companies operating in a closed market, has commented on the fact that this is an exceptionally easy course of action in the chemical industry, because of the similarity in scientific, technical, and merchandising problems of its different products. Competition in the chemical industry may come from other processes for producing the same commodity or from new materials striving for the same outlets, that is, inter-commodity or inter-process competition.<sup>147</sup> The technic of conducting commercial researches on chemical products, which usually requires the services of the laboratory as a weapon of offense and defense, has been discussed in some detail.<sup>148-150</sup> Other related subjects that have been treated are: chemical demand,<sup>151, 152</sup> seasonal variation,<sup>153</sup> customer research,<sup>154</sup> and technical servicing.<sup>155</sup>

**Distribution.** Considerable attention has been devoted in recent years, particularly by the Manufacturing Chemists' Association, to the development and standardization of suitable containers.<sup>156-159</sup> Questions of freight rates<sup>160</sup> and other distribution agencies<sup>161</sup> are of great importance in chemical marketing.

"For a hundred years," Haynes<sup>4</sup> points out, "the chemical industrialists of the world have been striving to make greater profits by paring down their raw material and plant costs, improving their yields, and increasing their sales volume. Every success has been but another incentive to greater sales effort. And additional sales effort has piled up selling expenses. Old markets have been more intensively cultivated. New markets have been invaded. The sales area has been widened, thus adding not only to direct sales cost but also to packing and transportation charges. . . . Better transportation and the desire of consumers to hold down their raw material inventories has meant smaller chemical orders and more frequent shipments. Expert advice—both practical technological help in operating problems and scientific assistance in research—is a part of the regular service a chemical seller is expected to render to his customers. Stimulated by a production program of ever increasing volume, the chemical sales executive is goaded by competition to extend his efforts beyond the limit of reason and fair profit.

"In this way distribution costs have climbed a steep spiral, but a situation so unsound economically is sure to be righted. It is quite logical, therefore, to find that marketing functions and policies are radically changing. As a result, distribution problems are today a chief concern of the industry."

The average plant cost of a chemical product may be estimated at 60 percent of the selling price.<sup>4, 162</sup> Freight equalization is said to account for 31.8 percent of the total sales expense of heavy chemicals.

Haynes<sup>4</sup> classifies marketing functions under the following headings: assembling, storing, grading, dividing, transporting, packing, selling, financing, and risking. "About 96 percent of our total production of

chemicals is consumed in industry and agriculture; but this indirect consumption of chemicals is not, from the marketing point of view, their most distinctive feature. Coal, iron and steel, copper, zinc and lead, wood, rubber, wool, silk, cotton, all enjoy widespread industrial markets; but none of them, as do chemicals, find their principal consuming field right within their own industry." The chemical industry consumes about 70 percent of all its products, either within the plant of their origin or as chemicals sold for use in further chemical processes.

The high intensity of competition in chemical marketing has been pointed out in several articles.<sup>168-169</sup> Technical aspects of sales policies, such as the 10th prox. discount<sup>170</sup> and the uniform sales contract<sup>171</sup> have been discussed. The rôle played by specification buying in the marketing of chemicals is important.<sup>172</sup> The various aspects of selling chemicals to the retail consumer have been analyzed.<sup>173</sup> The factors that play a part in sales costs have been pointed out.<sup>174</sup> There exists a problem of choosing between a sales policy based on marketing by products or one based on marketing by industries.<sup>175</sup> Beneficial effects on profits can be shown from an analysis of customers in their bearing on profitability.<sup>176</sup>

Haynes<sup>4</sup> has discussed the reasons for the non-existence of a Chemical Commodity Exchange. According to Smith,<sup>177</sup> the requisites for successful exchange trading are reasonable durability of commodities, accurate measurability, adequate standardization, sufficient volume, and comparatively high price fluctuations (inelastic supply). Haynes argues that while some chemicals may meet most or all of these requirements, chemicals in general as a class do not meet a single one; hence the organization of a chemical exchange is not a practical possibility.

Weld<sup>178</sup> quotes the following figures, compiled by the Association of National Advertisers, on the advertising expenditures of various industries.

TABLE III. *Average Advertising Expenditures of Various Industries Expressed in Percentage of Sales*

Drugs and toilet articles.....	19.6	Agricultural equipment and supplies .....	4.1
Paints and varnishes.....	6.4	Clothing .....	3.8
Chemical and allied manufactures .....	6.1	Furniture .....	3.7
Electrical and radio.....	5.9	Automotive .....	3.5
Jewelry and silverware.....	5.7	Leather and shoes.....	3.2
Food .....	5.6	Textiles .....	3.0
Office equipment and supplies	5.3	Building materials.....	2.8
Hardware .....	4.7	Paper and paper products....	2.6
Travel and transportation...	4.6	Metals, machinery, etc.....	2.5
Household equipment, other than electric.....	4.5	Industrial .....	2.3
		Finance and insurance.....	1.1

The successful use of radio programs as an advertising medium for fertilizers is described by Garrard.<sup>179</sup>

**Foreign Trade.** Weidlein and Bass,<sup>80</sup> summarizing the statistics

on foreign trade in products of the process industries, find a noteworthy increase in both exports and imports during the twenty years ending in 1929. In general, however, the volume of exports or imports is small compared with the production volume in this country for the same year, the average for exports of all manufactured products being 8.1 percent in 1929. Detailed reviews of our foreign trade in chemicals have been prepared by Wilson<sup>180</sup> and by the Chemical Division, Bureau of Foreign and Domestic Commerce.<sup>57</sup> Other aspects of foreign trade discussed include the tariff,<sup>22, 23</sup> measures of exports,<sup>181</sup> the effect of the chemical revolution,<sup>182</sup> and the South American export business.<sup>183</sup> The importance of the trend toward autarchy, or national self-sufficiency, has been discussed by Howard.<sup>184</sup>

**Accounting.** A chapter by Prochazka in the "Chemical Engineers' Handbook" <sup>78</sup> is devoted to accounting under the following headings: general accounting, analyzing financial statements, fixed-property accounting, cost accounting, process costs, material accounting, product costs, cost estimating, and budgeting. Articles have appeared on cost elements,<sup>185, 186</sup> costs from the point of view of the chemist or chemical engineer,<sup>187, 188</sup> "availability" in process steam cost accounting practice,<sup>189</sup> depreciation,<sup>127, 128, 190-192</sup> and budget control.<sup>193, 194</sup>

**Personnel.** Considerable attention has been given to the earnings of chemical engineering graduates.<sup>195-199</sup> The safety of chemical workers has aroused much consideration.<sup>200-204</sup> Women in chemistry,<sup>205</sup> chemists' contracts,<sup>206</sup> and the technic of applying for a position<sup>207</sup> have been discussed.

During periods of economic stress the larger industrial centers are confronted with difficult problems because of unemployment; this situation has focused attention on the problem of the relocation and development of new industries.<sup>208</sup> There should be a study of seasonal aspects of the chemical industries.<sup>209</sup> Technological unemployment has been much discussed.<sup>210, 211</sup>

**Financial Aspects.** Moulton,<sup>212</sup> in his comprehensive analysis of capital formation, observes that, in the years since the World War, the growth of capital in the chemical industry has shown the characteristics of a new industry. While increase in capital in established lines

TABLE IV. *Financing of New Industries in Millions of Dollars*

	1924	1925	1926	1927	1928	1929	1930
Aviation .....	...	1.9	...	0.2	55.1	172.8	4.2
Chemical .....	15.1	56.2	35.0	26.1	86.5	237.7	57.8
Motion picture.....	12.2	91.1	100.8	141.2	77.9	50.3	172.7
Natural gas.....	3.0	15.5	39.3	100.5	107.5	51.9	59.7
Radio .....	17.7	9.5	3.8	49.6	29.8	61.3	4.7

of manufacturing was relatively slow during this period, certain new lines of business, as shown in the following table, exhibited a rapid expansion in the later years of the boom period.

An analysis<sup>213</sup> of the \$4,101,000 of new financing in the chemical

industry since the Securities and Exchange Commission's activities began in October, 1934, discloses that \$300,000 was used for plant and equipment, \$531,000 for increased working capital, and \$3,175,000 for refinancing.

Weidlein and Bass,<sup>96</sup> analyzing the financial data compiled by Epstein<sup>214</sup> on 2,046 manufacturing corporations during the period 1919-1928, point out the following conclusions. The chemical industries show a low bonded debt in comparison with capitalization. They also show a capital ratio (ratio of capital invested to annual value of products) well above unity, confirming a similar observation made earlier by De Long.<sup>215</sup> The large sums received by chemical companies as dividends from other companies are a striking feature of the analysis.

The industry has been discussed by several writers from the point of view of general financial background and earnings.<sup>216-223</sup> The holdings of chemical securities in the portfolios of investment trusts have been analyzed.<sup>224</sup>

A comparison made by the National City Bank<sup>225, 226</sup> of figures for 1933 and 1934, from the annual reports of 18 of the larger chemical companies, reveals an increase in total net profits for the group from \$50,754,000 to \$64,165,000 or 26.4 percent. The total net worth of these companies remained approximately constant for these years, and, accordingly, the percentage return increased from 7.1 to 9.0.

**Industrial Organization.** During the early 1930's, there was considerable discussion of European cartels and their operation in periods of depression.<sup>4, 57, 227-229</sup> The organization of NRA and the introduction of the codes shifted interest to the American scene. The voices of the chemical industry were, in general, raised against the codes,<sup>230-240</sup> and following the adoption of the various governing codes,<sup>241-244</sup> there was much discussion of their effect, frequently of a sceptical nature.

The following interesting comment is made by Haynes<sup>5</sup> in regard to NRA: "When the NRA was launched General Johnson wanted employers to pay 40 cents an hour for 40 hours a week. But workers in chemical plants were already being paid 56½ cents for 41 hours. Today they receive 61.9 cents, or more than half again as much as the NRA ideal; and they work 39.4 hours a week."

**Individual Products.** In addition to publications of an economic nature relating to the industry as a whole, a number of valuable papers are concerned with some specific chemical or chemicals. Space does not permit detailed discussion, but for convenience a selected bibliography has been prepared. A large number of additional papers have been published on some of these products in journals specializing in their respective fields. Acetic acid and cellulose acetate,<sup>245, 246</sup> alcohol from wood waste,<sup>247</sup> alkalies,<sup>248, 249</sup> carbon black,<sup>250</sup> carbon dioxide,<sup>251</sup> foreign trade in copper,<sup>252</sup> fertilizers,<sup>253</sup> fuels,<sup>254</sup> hydrogen,<sup>255</sup> naval stores,<sup>256</sup> nitrogen,<sup>257-260</sup> petroleum,<sup>261</sup> phosphoric acid, phosphates and phosphate rock,<sup>262-265</sup> plastics,<sup>266</sup> potash,<sup>229, 267</sup> power alcohol and motor fuels,<sup>268-271</sup> pulp and paper,<sup>272</sup> rubber tires,<sup>273</sup> salt,<sup>274, 275</sup>

sugar,<sup>276, 277</sup> sulfur,<sup>278</sup> sulfuric acid,<sup>279, 280</sup> synthetic yarn,<sup>281</sup> tartaric acid.<sup>282</sup>

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